A

SYSTEMATIC HANDBOOK

OF

VOLUMETRIC ANALYSIS;

OR, brown

THE QUANTITATIVE DETERMINATION OF CHEMICAL SUBSTANCES BY MEASURE, APPLIED TO LIQUIDS, SOLIDS, AND GASES,

ADAPTED TO THE REQUIREMENTS OF PURE CHEMICAL RESEARCH, PATHOLOGICAL CHEMISTRY, PHARMACY, METALLURGY, MANUFACTURING CHEMISTRY, PHOTOGRAPHY, ETC., AND FOR THE VALUATION OF SUBSTANCES USED IN COMMERCE, AGRICULTURE, AND THE ARTS.

BY

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TENTH EDITION

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AUTHOR'S PREFACE.

An exceptionally long interval of seven years has elapsed since the publication of the last edition of this work, whilst it has been out of print for nearly eighteen months, a fact which is without precedent in its history. The interval has not left me a younger man, and I must confess that as the time for a new edition approached I have found myself, at the age of four-score years, less and less equal to the task. So large and so constant is the work now being done in the domain of volumetric analysis, that the need for reconsideration of old methods and of selection from amongst the newer methods becomes more imperative with each succeeding edition of a book of this character. The present, moreover, being the tenth edition, I was particularly anxious that it should be distinguished by the most thorough and critical revision yet attempted, and, in the result, by the greatest possible consonance with modern practice. To this end, I placed its preparation entirely in the hands of my son and partner, W. Lincolne Sutton, who had accumulated a large amount of material in anticipation, and of Mr. Alfred E. Johnson, author of the well-known "*Analyst's Laboratory Companion*," who had rendered me valuable and acknowledged assistance in the course of preparing the ninth edition. I feel that I cannot pay too generous a tribute to the devotion of both editors to the task they undertook. It has meant twelve months hard labour for each of them in the midst of exacting professional duties. I wish to record my gratitude especially to Mr. Johnson, who, without the hereditary interest of his co-editor, has worked

without reservation of time or trouble. He undertook the laborious task of critically revising the ninth edition line by line. I must admit that the result has rather damaged my conceit as an author, for it is obvious that many possible improvements will reveal themselves under a meticulate examination in a book which has grown, as this has, by a process of accretion tempered by pruning and extended through nine editions over a period of forty years. I am sensible that much remains to be done, but am sanguine enough to be looking forward already to the next and Jubilee edition, when the book will have attained its fiftieth year. A fresh opportunity will then present itself for moulding this, the least perishable work, I suppose, of my life, nearer my desire Meanwhile, I celebrate my jubilee as a Fellow of the Chemical Society with the present edition.

FRANCIS SUTTON.

NORWICH,
March, 1911.

EDITORS' PREFACE.

In preparing this edition, the ninth has been critically revised line by line, and the text slightly re-cast, added to, or considerably altered, as it seemed desirable in the interests of clearness, fulness of treatment, or accuracy. A good deal of obsolete matter has been deleted. For the sake of greater adaptability for constant use and reference in the laboratory, which has always been a valued feature of "Sutton," a new type has been selected, all references in the text have been carried to the foot of the page, and the page-headings have been amplified. For the same reason, we have endeavoured by compression and deletion not to increase the size of the book, in spite of the large amount of new matter inserted, and the present edition, in fact, does not differ from the last by more than a few pages. At the same time, great care has been taken not to alter in any way the general scope and original features of the work.

The International Atomic Weights for 1911 have been adopted throughout, and all factors, numerical examples, etc., recalculated accordingly. Special pains have been taken to show how the numerical results of analyses have been arrived at.

In Parts I. and II., the sections on the pipette, the measuring flask, and weights and measures, have been entirely re-written, the data used therein having been kindly supplied by Dr. R. J. Glazebrook, F.R.S., the Director of the National Physical Laboratory, to whom we gratefully tender our sincere thanks.

The term "normal solution" has been defined in, perhaps, a clearer manner, and fuller practical directions have been given for the preparation of the principal normal solutions in common use. The section on Indicators has been somewhat amplified and that dealing with the titration of mixed alkali salts has been partially re-cast and re-written for the sake of greater clearness. The most recent procedure for the technically complete analysis of ammoniacal liquors, as published in the Annual Report for 1909 of the Chief Inspector under the Alkali etc. Works Regulation Act, has been substituted for that given in the last edition. In this connexion our best thanks are due to Mr. Forbes Carpenter, the Chief Alkali Works Inspector, and Mr. Linder, his assistant. Many other sections in these two parts have been considerably altered, re-written, or added to.

The introductory portion of Part III. has been re-written and the subject matter considerably amplified. Part IV. is short (pp. 141-147), and has undergone but little alteration.

In Part V. (pp. 148-420) the alterations have been so numerous and important that attention can be directed only to a few of them. The section on ferrocyanides has been entirely re-written, much expanded, and brought up to date; Knecht's latest process for the titration of iron by titanous chloride has been described; the determination of sulphur in iron and steel as carried out at the National Physical Laboratory is included; under Magnesium, Manganese, Mercury and Nickel several new processes are given. The section on Dissolved Oxygen has been greatly enlarged. Portions of the section on Sugars have been re-written, and Mr. A. R. Ling has kindly contributed an account of his most recent methods of procedure in the use of Fehling's solution. Important new matter is given under Titanium, Vanadium, and Zinc. The article on Acetone has been entirely re-written and the Government Specification inserted. We are indebted to the Director of Artillery, Royal Gunpowder Factory, Waltham Abbey, for kindly furnishing the latter. Under "Oils, Fats and Waxes"

numerous portions of the text have been re-written, worked examples added, and a description of the Polenske method, with figure, inserted. Phenols and Cresols have also received attention.

In Part VI. Liebig's method for determination of urea has been deleted and Gerrard's apparatus described. The Water and Sewage Section has been most thoroughly revised and re-arranged, with numerous additions, including a special index to the section.

Beyond numerical and typographical revision, little change has been made in the Gas Analysis section.

For the loan of blocks we desire to thank Messrs. Macmillan (fig. 57a), the publishers of Lewkowitsch's "*Oils, Fats and Waxes*"; Messrs. Longmans (fig. 55), the publishers of Knecht and Hibbert's "*New Reduction Methods in Volumetric Analysis*"; and Messrs. Churchill (fig. 59), publishers of Allen's "*Chemistry of Urine.*"

W. L. S.

A. E. J.

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MEMORANDA.

WEIGHTS AND MEASURES.

(See p. 23.)

1 metre	=	39·370113 inches.
,,	=	3·280843 feet.
1 gram (gm.)	=	15·43236 grains (grs.).
1 kilogram	=	2·2046 lb. avoirdupois.

The standard litre is the volume of a kilogram of pure water at 4° C. under standard barometric pressure.

1 litre	=	1000·028 cubic centimetres.
,,	=	1·75980 pints.
,,	=	0·219975 gallon.

1 litre of water at 15° C. weighs 999·13 grams.

TEMPERATURE.

The usual standard temperature for graduated vessels and standard solutions used in volumetric analysis is 15° C. (=59° F.). For special purposes, however, other temperatures are also in common use (see p. 25).

NORMAL SOLUTIONS.

A normal solution of a reagent is one that contains in a litre that proportion of its molecular weight in grams which corresponds to one gram of available hydrogen or its equivalent (see p. 28). Decinormal ($^{N}/_{10}$) and centinormal ($^{N}/_{100}$) solutions are respectively of one-tenth and one-hundredth of this strength.

By means of a standard solution, a given volume of which has been proved to be equivalent to a known amount of a certain substance, the quantity of such substance contained in a given quantity of another solid or liquid body can be determined. This process is termed *titration*.

ABBREVIATIONS USED.

Ber.	=	Berichte der deutschen chemischen Gesellschaft.
C. N.	=	Chemical News.
J. A. C. S.	=	Journal of the American Chemical Society.
J. C. S.	=	Journal of the Chemical Society.
J. S. C. I.	=	Journal of the Society of Chemical Industry.
Z. a. C.	=	Zeitschrift für analytische Chemie.
Z. f. angew. C.	=	,, ,, angewandte ,,

ABRIDGED LIST OF THE

INTERNATIONAL ATOMIC WEIGHTS FOR 1911

(used throughout this work).

		$O=16$.			$O=16$.
Aluminium	Al	27·1	Magnesium	Mg	24·32
Antimony	Sb	120·2	Manganese	Mn	54·93
Arsenic	As	74·96	Mercury	Hg	200
Barium	Ba	137·37	Molybdenum	Mo	96
Bismuth	Bi	208	Nickel	Ni	58·68
Boron	B	11	Nitrogen	N	14·01
Bromine	Br	79·92	Oxygen	O	16
Cadmium	Cd	112·4	Palladium	Pd	106·7
Calcium	Ca	40·09	Phosphorus	P	31·04
Carbon	C	12	Platinum	Pt	195·2
Cerium	Ce	140·25	Potassium	K	39·1
Chlorine	Cl	35·46	Silicon	Si	28·3
Chromium	Cr	52	Silver	Ag	107·88
Cobalt	Co	58·97	Sodium	Na	23
Copper	Cu	63·57	Strontium	Sr	87·63
Fluorine	F	19	Sulphur	S	32·07
Gold	Au	197·2	Tin	Sn	119
Hydrogen	H	1·008	Titanium	Ti	48·1
Iodine	I	126·92	Tungsten	W	184
Iron	Fe	55·85	Uranium	U	238·5
Lead	Pb	207·1	Vanadium	V	51·06
Lithium	Li	6·94	Zinc	Zn	65·37

VOLUMETRIC ANALYSIS

OF

LIQUIDS AND SOLIDS.

PART I.

GENERAL PRINCIPLES.

QUANTITATIVE analysis by weight, or gravimetric analysis, consists in separating out the constituents of any compound, either in a pure state or in the form of some new substance of known composition, and accurately weighing the products. Such operations are frequently very complicated, and occupy a long time, besides requiring in many cases elaborate apparatus, and the exercise of much care and experimental knowledge. Volumetric processes on the other hand, are, as a rule, quickly performed ; in most cases are susceptible of extreme accuracy, and need much simpler apparatus. The leading principle of the method consists in submitting the substance to be determined to certain characteristic reactions, employing for such reactions solutions of known strength, and from the volume of solution necessary for the production of such reaction calculating the weight of the substance to be determined by aid of the known laws of chemical equivalence.

Volumetric analysis, or quantitative chemical analysis by measure, in the case of liquids and solids, consequently depends upon the following conditions for its successful practice :—

1. A solution of the reagent, the chemical value of which is accurately known, called the " standard solution."

2. A graduated vessel from which portions of it may be accurately delivered, called the " burette."

3. The decomposition produced by the standard solution with any given substance must either in itself or by an indicator be such, that *its termination is unmistakable to the eye*, and thereby the

quantity of the substance with which it has combined accurately calculated.

Suppose, for instance, that it is desired to know the quantity of pure silver contained in a shilling. The coin is first dissolved in nitric acid, by which means a bluish solution, containing silver, copper, and probably other metals, is obtained. It is a known fact that chlorine combines with silver in the presence of other metals to form silver chloride, which is insoluble in nitric acid. The proportions in which the combination takes place are 35·46 of chlorine to every 107·88 of silver; consequently, if a standard solution of pure sodium chloride is prepared by dissolving in water such a weight of the salt as will be equivalent to 35·46 grains of chlorine (=58·46 grains NaCl) and diluting to the measure of 1000 grains, every single grain measure of this solution will combine with 0·10788 grain of pure silver to form silver chloride, which is precipitated to the bottom of the vessel in which the mixture is made. In the process of adding the salt solution to the silver, drop by drop, a point is at last reached when the precipitate ceases to form. Here the process must stop. On looking carefully at the graduated vessel from which the standard solution has been used, the operator sees at once the number of grain measures which has been necessary to produce complete decomposition. For example, suppose the quantity used was 520 grain measures; all that is necessary to be done is to multiply 520 by the coefficient for each grain measure, viz. 0·10788, which shows the amount of pure silver present to be 56·098 grains.

This method of determining the quantity of silver in any given solution occupies scarcely a quarter of an hour, whereas the determination by weighing could not be done in half a day, and even then not so accurately as by the volumetric method. It must be understood that there are certain necessary precautions in conducting the above process which have not been described; those will be found in their proper place; but from this example it will at once be seen that the saving of time and trouble, as compared with the older methods of analysis, is immense; besides which, in the majority of instances in which it can be applied, it is equally accurate, and in many cases much more so.

The only conditions on which the volumetric system of analysis can be carried on successfully are that great care is taken with respect to the graduation of the measuring instruments, and their agreement with each other, the strength and purity of the standard solutions, and the absence of other matters which would interfere with the accurate determination of the particular substance sought.

The fundamental distinction between gravimetric and volumetric analysis is that, in the former method, the substance to be determined must be completely isolated in the purest possible state or combination, necessitating in many instances very patient and discriminating labour; whereas, in volumetric processes, such complete separation is very seldom required, the processes being so

contrived as to admit of the presence of half a dozen or more other substances which have no effect upon the particular chemical reaction required.

The process just described for instance, the determination of silver in coin, is a case in point. The alloy consists of silver and copper, with small proportions of lead, antimony, tin, gold, etc. None of these metals affect the amount of salt solution which is chemically required to precipitate the silver, whereas, if the metal had to be determined by weight it would be necessary first to filter the nitric acid solution to free it from insoluble tin, gold, etc. ; then precipitate with a slight excess of sodium chloride ; then to bring the precipitate upon a filter, and wash repeatedly with pure water until every trace of copper, salt, etc., is removed. The pure silver chloride is then carefully dried, ignited separately from the filter, and weighed ; the filter burnt, the residue as reduced metallic silver and filter ash allowed for, and thus finally the amount of silver is found by the balance with ordinary weights.

On the other hand the volumetric process has been purely chemical, the burette or measuring instrument has taken the place of the balance, and theoretical or atomic weights have supplanted ordinary weights.

The end of the operation in this method of analysis is in all cases made apparent to the eye. In alkalimetry it is the change of colour produced in litmus, turmeric, or other sensitive colouring matter. The formation of a permanent precipitate, as in the determination of cyanogen. A precipitate ceasing to form, as in chlorine and silver determination. The appearance of a distinct colour, as in iron analysis by permanganate solution, and so on.

I have adopted the classification of methods used by Mohr and others, namely :

1. Where the determination of the substance is effected by saturation with another substance of opposite properties—generally understood to include acids and alkalies and alkaline earths.

2. Where the determination of a substance is effected by a reducing or oxidizing agent of known power, including most metals, with their oxides and salts. The principal oxidizing agents are potassium permanganate, potassium dichromate, and iodine ; and the corresponding reducing agents, ferrous and stannous compounds, and sodium thiosulphate.

3. Where the determination of a substance is effected by precipitating it in some insoluble and definite combination, an example of which occurs in the determination of silver described above.

This classification does not completely include all the volumetric processes that may be used, but it divides them into convenient sections for describing the peculiarity of the reagents used, and their preparation. If strictly followed out, it would in some cases necessitate the registration of the body to be determined under two or three heads. Copper, for instance, can be determined residually by permanganate ; it can also be determined by

precipitation with sodium sulphide. The determination of the same metal by potassium cyanide, on the other hand, would not come under any of the above heads.

It will be found, therefore, that liberties have been taken with the arrangement; and for convenient reference all analytical processes applicable to a given body are included under its name.

It may be a matter of surprise to some that several distinct volumetric methods for one and the same substance are given; but a little consideration will show that in many instances greater convenience, and also accuracy, may be gained in this way. The operator may not have one particular reagent at command, or he may have to deal with such a mixture of substances as to preclude the use of some one method; whereas another method may be quite free from such objection. The choice in such cases of course requires judgment, and it is of the greatest importance that the operator should be acquainted with the qualitative composition of the matters with which he is dealing, and that he should ask himself at every step why such and such a thing is to be done.

It will be apparent from the foregoing description of the volumetric system that it may be successfully used in many instances by those who have never been thoroughly trained as analytical chemists; but we can never look for the scientific development of the system in such hands as these.

In the preparation of this work an endeavour has been made to describe all the operations and chemical reactions as simply as possible, all the necessary calculations being made as far as possible without the aid of long mathematical formulae and requiring usually nothing further than a knowledge of the ordinary rules of arithmetic and occasionally of elementary algebra.

THE INSTRUMENTS AND APPARATUS.

THE BALANCE.

STRICTLY speaking, it is necessary to have two balances in order to carry out completely the volumetric system. One to carry about a kilogram in each pan and to turn when fully loaded with about 5 milligrams ; the other to carry about 50 grams and to turn easily and quickly, when fully loaded, with one- or two-tenths of a milligram. The former instrument is used for weighing large amounts of pure reagents in the preparation of standard solutions, and for making the necessary weighings when graduating or testing measuring flasks. The latter instrument, which must be of much lighter construction, serves for weighing small quantities of substances to be tested, many of which, being hygroscopic, need weighing quickly as well as accurately, also for the delicate weighings required when testing the accuracy of pipettes and burettes.

For all technical purposes, however, a moderate-sized balance of medium delicacy is quite sufficient, especially if rather large quantities of substances are weighed and brought into solution—then further subdivided by means of measuring flasks and pipettes.

The operator also requires, besides the balance and graduated instruments, a few beakers, porcelain basins, flasks, funnels, stirring rods, etc., as in gravimetric analysis. Above all, he must be practically familiar with proper methods of filtration, washing of precipitates, and the application of heat.

VOLUMETRIC ANALYSIS WITHOUT WEIGHTS.

THIS is more a matter of curiosity than of value ; but, nevertheless, one can imagine circumstances in which it might be useful. In carrying it out, it is necessary only to have (1) a correct balance, (2) a pure specimen of substance to use as a weight, (3) an accurate burette filled with the appropriate solution. It is not necessary that the strength of this should be known ; but the state of concentration should be such as to permit the necessary reaction to occur under the most favourable circumstances.

If a perfectly pure specimen of substance, say calcium carbonate, be put into one scale of the balance, and be counterpoised with an impure specimen of the same substance, and both titrated with the same acid, and the number of c.c. used for the pure substance be called 100, the number of c.c. used for the impure substance will correspond to the percentage of pure calcium carbonate in the specimen examined.

The application of the process is, of course, limited to the use of such substances as are to be had pure, and whose weight is not variable by exposure ; but where even a pure substance of one kind

cannot be had as a weight, one of another kind may be used as a substitute, and the required result obtained by calculation. For instance, it is required to ascertain the purity of a specimen of sodium carbonate, and only pure calcium carbonate is at hand to use as a weight; equal weights of the two are taken, and the impure specimen titrated with acid. To arrive at the required result, it is necessary to find a coefficient or factor by which to convert the number of c.c. required by the sodium carbonate, weighed on the calcium, into that which should be required if weighed on the sodium, basis. A consideration of the relative molecular weights of the two bodies will give the factor thus—

$$\frac{\text{Calcium carbonate } 100{\cdot}09}{\text{Sodium carbonate } \quad 106} = 0{\cdot}9443$$

If, therefore, the c.c. used are multiplied by this number, the percentage of pure sodium carbonate will be obtained. On this principle, and with the exercise of a little ingenuity, the analysis of a number of substances may be carried out.

L. de Koningh has communicated to me a similar method devised by himself and Peacock, in which the same end is attained without the aid of a pure substance as standard, thus: Say a specimen of impure common salt is to be examined. A moderate portion is put on the balance and counterpoised with silver nitrate; the latter is then dissolved in water, made up to 100 c.c. and placed in a burette. The salt is dissolved in water, a few drops of potassium chromate added and titrated with the silver solution, of which 10 c.c. is required; the salt is therefore equal to 10 per cent. of its weight of silver nitrate, then—

$$16{\cdot}99 : 58{\cdot}46 :: 10 = 3{\cdot}44 \ \% \ NaCl$$

Or, in the case of an impure soda ash, an equal weight of oxalic acid is taken and made up to 100 c.c.; the soda requires, say, 50 c.c. for saturation, or 50 per cent., then—

$$126 : 106 :: 50 = 42 \ \% \ Na_2CO_3$$

It may happen that, in some cases, more than one portion of the reagent is required to decompose the substance titrated, and to provide against this two or more lots should be weighed in the first instance.

VOLUMETRIC ANALYSIS WITHOUT BURETTES OR OTHER GRADUATED INSTRUMENTS.

This operation consists in weighing the standard solutions on the balance instead of measuring them. The influence of variation in temperature is, of course, here of no consequence. The chief requisite is a delicate flask, fitted with a tube and blowing ball, as in the burette fig. 7, or an instrument known as Schuster's alkalimeter may be used. A special burette has been devised for

this purpose by Casamajor*. The method is capable of very accurate results, if care be taken in preparing the standard solutions and avoiding any loss in pouring the liquid from the vessel in which it is weighed. It occupies much more time than the usual processes of volumetric analysis, but at great extremes of temperature it is far more accurate.

THE BURETTE.

THIS instrument is used for the delivery of an accurately measured quantity of any particular standard solution. It invariably consists of a long glass tube of even bore, throughout the length of which are engraved, by means of hydrofluoric acid, certain divisions corresponding to a known volume of fluid.

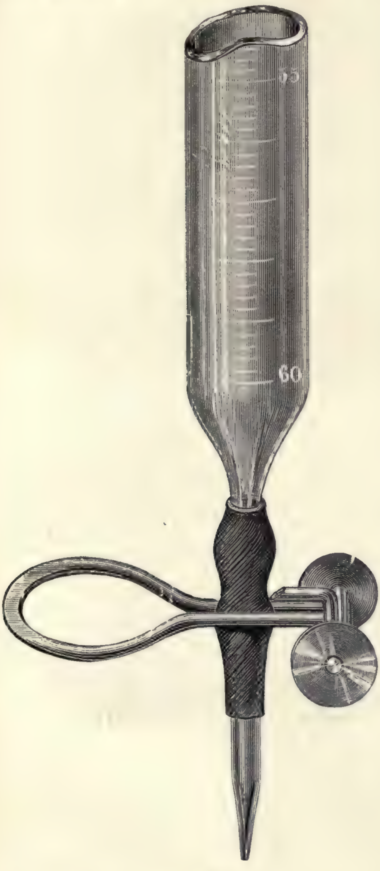


Fig. 1.

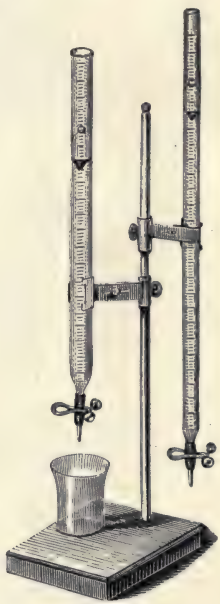


Fig. 2.

It may be obtained in a great many forms, under the names of

* *C. N.* **35**, 98.

their respective inventors, such as Mohr, Gay Lussac, Bink, etc., but as some of these possess a decided superiority over others it is not quite a matter of indifference which is used, and therefore a slight description of them may not be out of place here. The burette, with india-rubber tube and clip, contrived by Mohr, is shown in figs. 1 and 2, and, with glass stop-cock, in fig 3. This latter form of instrument is now made and sold at such a moderate price that it has largely displaced the original form designed by Mohr.

A further improvement in modern graduated instruments applied to burettes, thermometers, etc., is a strip of milk glass in the tube, behind the graduation marks and figures, which are filled with black varnish to render them conspicuous.

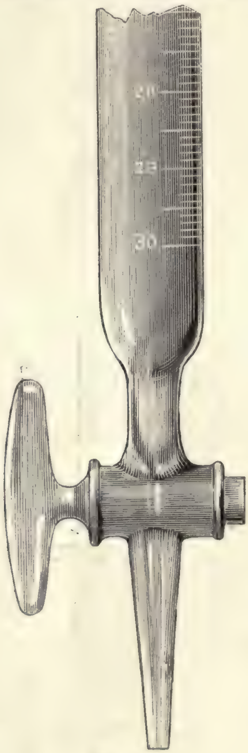


Fig. 3.

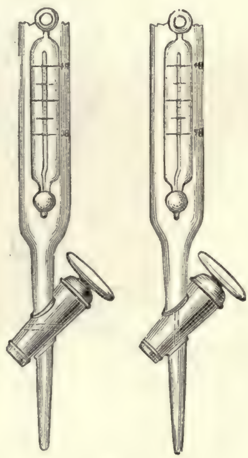


Fig. 4.

The advantages possessed by Mohr's burette are as follows: Its fixed upright position in a stand enables the operator at once to read off the volume of a standard solution used; the quantity of liquid to be delivered can be regulated to the greatest nicety; and, not being touched by the hand, the volume of the liquid cannot be increased by the heat of the body, as is often the case with

Bink's or Gay Lussac's burette. The principal disadvantage of these two latter forms, however, is that a correct reading in each case can only be obtained by placing the instrument in an upright position and allowing the fluid to find its proper level. The preference, therefore, should unhesitatingly be given to Mohr's burette. The tap burette may be used not only for solutions affected by the rubber tube, but for all other solutions, and may also be arranged so as to deliver the liquid in drops, leaving both the hands of the operator disengaged. A new arrangement is shown in fig. 4, the tap being placed obliquely through the jet, so as to avoid its dropping out of place; the floats shown are very small

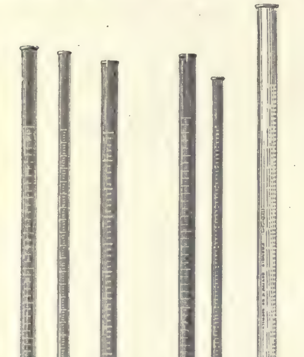


Fig. 5.

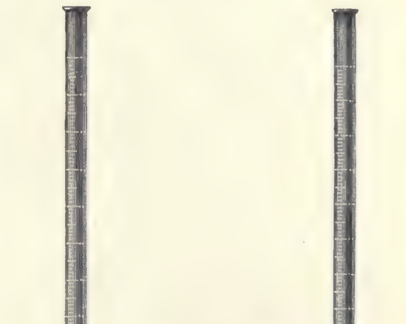


Fig. 6.

thermometers. Owing to the action of caustic alkalies upon glass, tap burettes do not answer well for strong solutions of potash or soda, unless emptied and washed immediately after use. A very good modification of this burette, as usually made, is to have the top funnel-shaped. This not only admits of more easy filling, but enables the burette to be hung on a stand by the funnel without other support and also to be tilted from the vertical when titrating

hot solutions. When not in use, the dust may be kept out of such a burette by a greased glass plate. Ordinary burettes should be covered with an inverted test-tube when not in use. Two convenient forms of stand for Mohr's burettes are shown in figs. 5 and 6. In the former the arms carrying the burettes revolve.

Special care should always be taken with Mohr's form of burette to fill the delivery point of the instrument and the intervening rubber tube with the liquid, before commencing a titration. This is easily done by filling the burette well above the 0 mark, then rapidly opening the clip wide to expel the air bubbles. When this is done, the excess of liquid may be quietly run out to the mark. In the tap burette the air space is smaller than with the rubber tube, but the same method should be invariably adopted. Glass taps should be occasionally smeared with a small quantity of vaseline as lubricant. A thin ring of india-rubber tubing stretched over the projecting narrow end of the tap is useful for keeping it in position.

We are indebted to Mohr for another form of instrument to avoid the contact of permanganate and india-rubber, viz., the foot burette, with elastic ball, shown in fig. 7.

The flow of liquid from the exit tube can be regulated to a great nicety by pressure upon the ball, which should be large, and have two openings,—one cemented to the tube with marine glue, and the other at the side, over which the thumb is placed when pressed, and on the removal of which it refills with air.

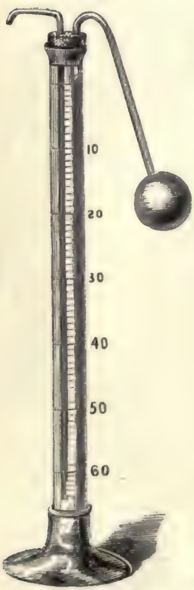


Fig. 7.


Fig. 8.

Gay Lussac's burette, supported in a wooden foot, may be used instead of the above form by inserting into the open end a good fitting cork, through which a small tube bent at right-angles is passed. If the burette is held in the right hand, slightly inclined towards the beaker or flask into which the fluid is to be measured, and the mouth applied to the tube, any portion of the solution may be emptied out by the pressure of the breath, and the disadvantage of holding the instrument in a horizontal position, to the great danger of spilling the contents, is avoided; at the same time the beaker or flask can be held in the left hand and shaken so as to mix the fluids, and by this means the end of the operation be more accurately determined (see fig. 8).

There is an arrangement of Mohr's burette which is extremely serviceable when a series of titrations of the same character have to be made, such as in alkali works, assay offices, etc. It consists in having a ⊤ piece of glass tube inserted between the lower end of the burette and the spring clip, communicating with a reservoir of the standard solution placed above, so that the burette may be filled by a siphon as often as emptied, and in so gradual a manner that no air bubbles are formed, as when filling it with a funnel or pouring in liquid from a bottle. This arrangement has the additional advantage of preventing evaporation of the standard solution either in the burette or the reservoir, and also keeps out dust.

Figs. 9 and 11 show this arrangement in detail. Connections of this kind may now be had with glass stop-cocks, either of the simple form or the patent two-way cock, made by Greiner and Friedrichs, and supplied by most apparatus dealers (fig. 10).

Fig. 9.

Fig. 10.

It sometimes happens that a solution requires titration at a hot or even boiling temperature, such as the determination of sugar by

copper solution: here the ordinary arrangement of Mohr's burette will not be available, since the steam rising from the liquid heats the burette and alters the volume of fluid. This may be avoided either by using a special burette, in which the lower end is extended at a right-angle with a stop-cock, or by attaching to an ordinary burette a much longer piece of india-rubber tube, so that the burette stands at the side of the capsule or beaker being heated, and the elastic tube is brought over its edge, the pinch-cock being fixed midway. No heat can then reach the body of fluid in the burette, since there can be no conduction past the pinch-cock. A burette

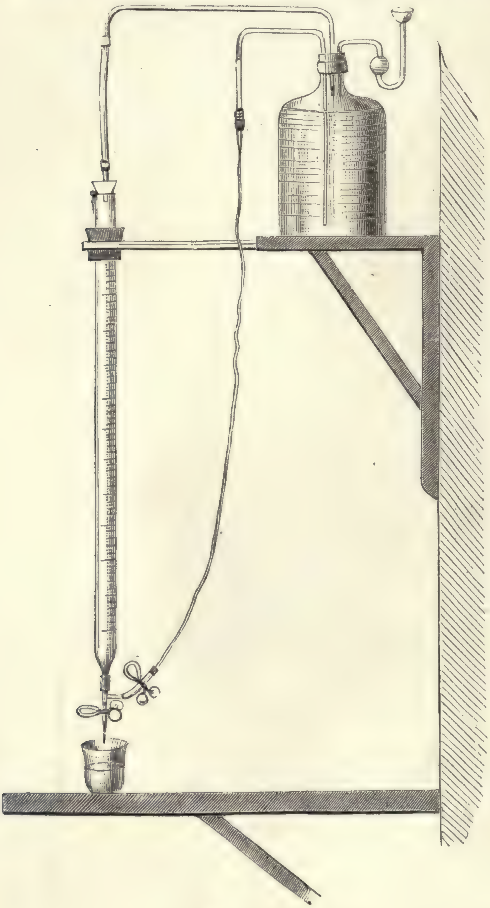


Fig. 11.

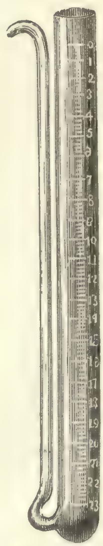


Fig. 12.

with funnel neck as described on page 9 may also be used for this purpose.

Gay Lussac's burette is shown in figs. 8 and 12. By using it in

the following manner its inherent disadvantages may be overcome to a great extent. Having fixed the burette into the foot securely, and filled it, take it up by the foot, and resting the upper end upon the edge of the beaker containing the solution to be titrated drop the test fluid from the burette, meanwhile stirring the contents of the beaker with a glass rod; by a slight elevation or depression the flow of test liquid is regulated until the end of the operation is secured. In this way the annoyances which arise from alternately placing the instrument in an upright and a horizontal position are avoided.

Bink's burette is well known, and need not be described; it is the least recommendable of all forms, except for very rough estimations.

It is convenient to have burettes graduated to contain from 30 to 50 c.c. in $\frac{1}{10}$ c.c. and 100 or 110 c.c. in $\frac{1}{5}$ or $\frac{1}{2}$ c.c.

The pinch-cock generally used in Mohr's burette is shown in fig. 1. These are made of brass and are now generally nickel-plated to prevent corrosion. Another form is made of one piece of steel wire, as devised by Hart; the wire is softened by heating, and coiled round as shown in fig. 13. When the proper shape has been attained, the clip is hardened and tempered so as to convert it into a spring.

Another pinch-cock is shown in fig. 13. It may be made of hard wood, horn, or, preferably, of flat glass rod. The levers should be long. A small piece of cork, of the same thickness as the elastic tube of the burette when pressed close, should be fastened at the angles of the levers as shown in the engraving.

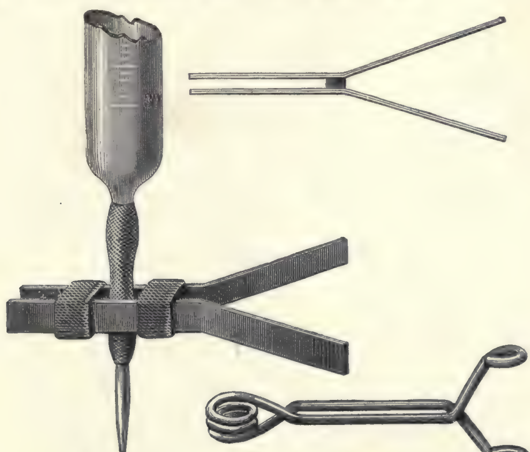


Fig. 13.

The use of any kind of pinch-cock may be avoided, and a very delicate action obtained, by simply inserting a not too tightly fitting piece of solid glass rod into the elastic tube between the end of the

burette and the jet. A firm squeeze being given by the finger and thumb to the elastic tube surrounding the rod, a small canal is opened, and thus the liquid escapes, and of course can be controlled by the operator at will (see fig. 14).

THE PIPETTE.

The pipettes used in volumetric analysis are of two kinds: (1) whole pipettes, which have but one mark and deliver a fixed quantity marked on the measure; (2) graduated pipettes, the stems

Fig. 14.

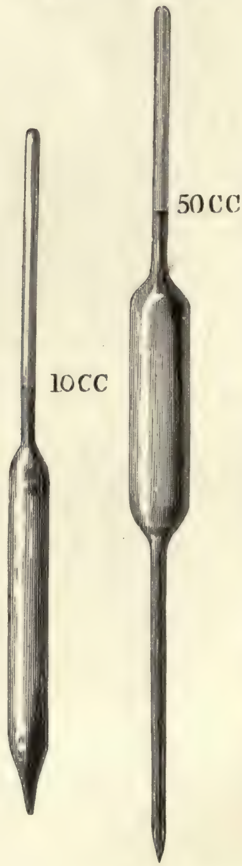


Fig. 15.

Fig. 16.

of which are graduated to deliver various quantities at the discretion of the analyst. In using the former, they are first filled from the jet to about 1 cm. above the mark, then allowed to run down just to the mark. Any drops adhering to the jet are removed. The liquid is then allowed to run out into the vessel where it is required,

the point of the jet touching the wall of the vessel. After the continuous outflow has ceased, the pipette is allowed to drain for 15 seconds and the jet is then stroked off the wall of the vessel. The "Limits of Error" allowed in pipettes standardized at the National Physical Laboratory are as follows :—

Limits of Error in c.c.

For c.c. inclusive	2	10	30	75	200
c.c.	·01	·02	·03	·05	·1

The standard temperature is 15° C.

In all pipettes, the upper end is narrowed to about $\frac{1}{8}$ inch, so that the pressure of the finger is sufficient to arrest the flow at any point.

Pipettes are invariably filled by sucking the upper end with the mouth, unless the liquid is volatile or highly poisonous, in which case it is best to use some other kind of measurement. Beginners invariably find a difficulty in quickly filling the pipette above the mark, and stopping the fluid at the exact point. Practice with pure water is the only method of overcoming this.

Fig. 15 shows two whole pipettes, one of small and the other of large capacity, and also a graduated pipette of medium size. It must be borne in mind that the pipette graduated throughout the stem is not a reliable instrument for accurate titration, owing to the difficulty of stopping the flow of liquid at any given point and reading off the exact measurement. Its chief use is in the approximate determination of the strength of any standard solution in the course of preparation.

Fig. 16 shows a very useful form of pipette for measuring strong acids or alkalies, etc., the bulb preventing the entrance of any liquid into the mouth.

THE MEASURING FLASK.

Measuring flasks serve to make up standard solutions to a given volume, and also enable the analyst, with the aid of pipettes, to obtain aliquot portions of a substance to be tested. They should be as narrow in the neck as is compatible with easy filling and emptying, and the mark should be situated below the middle of the neck, so as to allow room for thoroughly mixing the contents by shaking.

Measuring flasks are made either to *contain* or to *deliver* the quantities marked on them, and the temperature at which they have been standardized should invariably be marked on also. Ordinary flasks with one mark are always taken to *contain* the amount specified. Vessels standardized at the National Physical Laboratory, Teddington, are marked with the letter D when they are meant to deliver; if meant for both content and delivery the letter D is placed above the upper, and the letter C below the lower, mark. The standard temperature is 15° C. Thus, a standardized flask marked "1 litre 15° C." is such that, at a temperature of 15° C., the volume of the contents of the flask is the

same as that of a kilogram of water at a temperature of 4° C. Since, however, the density of water at 15° C. is 0·99913 grams per c.cm., the weight of water at 15° C. which fills the flask up to the mark is 999·13 grams, not 1000 grams.

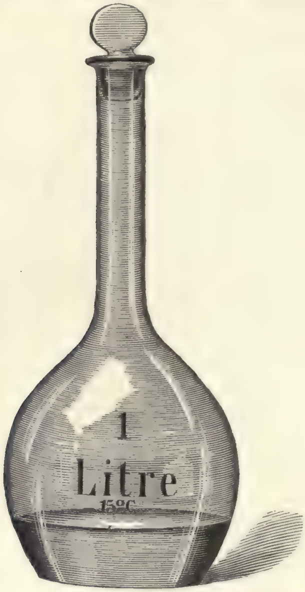


Fig. 17.

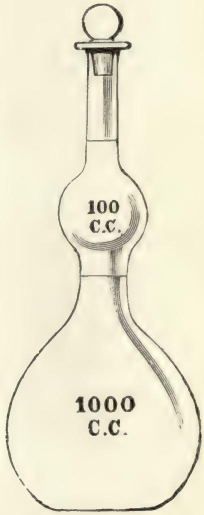


Fig. 18.

Volumetric measures standardized at Charlottenburg are marked with the letters A and E to indicate "deliver" and "contain" respectively, these being the initial letters of the words "Ausguss" and "Einguss," signifying pouring out and pouring in.

As examples of the "Limits of Error" observed at the National Physical Laboratory the following may be given :—

Measuring Flasks.
Limits of Error in c.c.

For c.c.	50	100 to 250	300 to 500	550 to 1000	2000
c.c. to contain	·05	·1	·15	·3	·5
c.c. to deliver	·1	·2	·3	·6	1·0

The German limits are practically the same.

Measuring flasks are ordinarily made of 50, 70, 100, 200, 250, 500, 1000 and 2000 c.c. capacity. Flasks for delivery should be gradually tilted till nearly vertical, drained for one minute, and the last drop removed by touching the side of the vessel into which they are being emptied.

W. B. Giles has described a modified flask*, shown in fig. 18. It is handy in making up standard solutions where the reagent cannot be weighed in an absolutely pure state, for instance, sulphuric

* *C. N.* **69**, 99.

acid, ammonium thiocyanate, or uranic salts. Such a quantity, however, is taken as will give a solution about a ninth or tenth too strong, and the measure is made up to 1100 c.c. The real strength is then taken by two titrations on 25 or 30 c.c. with a known standard, so that its exact working strength is known; the remainder of the 100 c.c. is then removed down to the 1000 c.c. mark, and a slight calculation will show how much water has to be added to the 1000 c.c. to make a correct solution. If only a litre is made up, an unknown volume is left in the flask, and it must be transferred to a measuring cylinder, where, owing to the large diameter of the vessel, the graduation can never be so accurate as in the narrow neck of the flask. Should the solution prove to be only about a tenth too strong, the necessary dilution may be made in the flask itself; but if stronger than this, the flask must be emptied into the store bottle and rinsed out with the measured quantity of water required, which is then drained into the store bottle, and the whole carefully mixed.

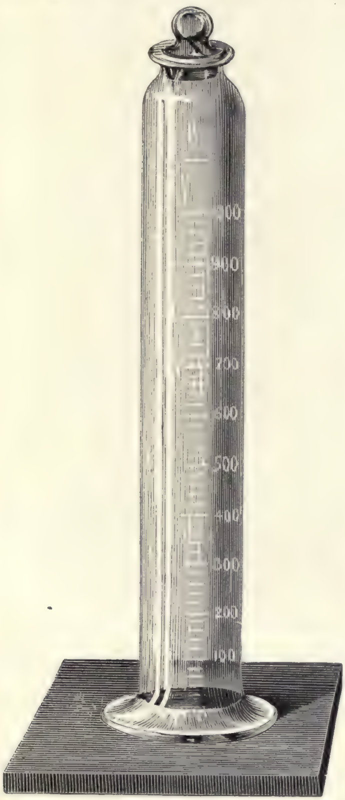


Fig. 19.

In addition to the measuring flasks it is necessary to have graduated vessels of cylindrical form for the purpose of preparing standard solutions, etc.

Fig. 19 shows a stoppered cylinder for this purpose, generally called a test mixer. Wide-mouthed open cylinders, with spouts, of various sizes and graduated like fig. 19, are also used.

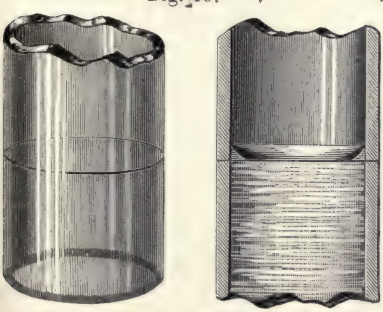


Fig. 20.

ON THE CORRECT READING OF GRADUATED INSTRUMENTS.

In consequence of capillarity the surface of liquids in narrow tubes is always curved. Where the liquid wets the tube, its surface

takes the form of a meniscus which is concave, as shown in fig. 20. In reading the heights of such liquids in tubes, the point where a graduation mark coincides with the bottom of the curve is taken.

The eye may be assisted materially in reading the divisions on a graduated tube by using a piece of white paper or opal glass held at an angle of 30° or 40° from the burette and near the surface of the liquid, or a small card, the lower half of which is blackened, the upper remaining white. If the line of division between the black and white be held about an eighth of an inch below the surface of the liquid, and the eye brought on a level with it, the meniscus can then be seen by transmitted light, bounded below by a sharply defined black line. A card of this kind, sliding up and down a support, is of great use in verifying the graduation of the burettes or pipettes with a cathetometer. Another good method is to use a piece of mirror, upon which are gummed two strips of black paper, half an inch apart; apply it in contact with the burette so that the eye can be reflected in the open space. The operator may consult with advantage the directions for calibration on the following page, and details of graduating and verifying measuring instruments for the analysis of gases as described in Part 7. In taking the readings of burettes, pipettes, and flasks, the graduation mark should coincide as nearly as possible with the level of the operator's eye.

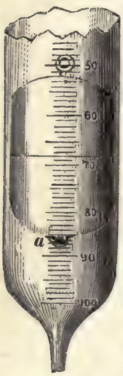


Fig. 21.

Erdmann's Float.—This useful little instrument to accompany Mohr's burette, gives the most accurate reading that can be obtained; one of its forms is shown in fig. 21, another, containing a thermometer, is shown in fig. 4. The latest form is shown in fig. 22, where the ring-mark is made within the bulb, as indeed it is best to be in all cases. A special form for use with dark-coloured solutions like iodine, permanganate, etc., is to have two bulbs with the ring-mark in the upper bulb, and the instrument is so weighted that the upper bulb stands out of the liquid, and of course may then be read off as easily as if the liquid were transparent. The instrument consists essentially of an elongated glass tube, rather smaller in diameter than the burette itself, and weighted at the lower end with a globule of mercury. The actual height of the liquid in the burette is not regarded, because if the operator begins with the line on the float opposite the 0 graduation mark on the burette the same proportional division is always maintained.


Fig. 22.

It is essential that the float should move up and down in the burette without wavering, and the line upon it should always be parallel to the graduations of the burette.


Fig. 23.

Filter for ascertaining the end-reaction in certain processes.—This is shown in fig. 23, and the instrument is known as Beale's filter. It serves well for taking a few drops of clear solution from any liquid in which a precipitate will not settle readily. To use it, a piece of filter paper is tied over the lower end, and over that a piece of fine muslin to keep the paper from being broken. When dipped into a muddy mixture, the clear fluid rises and may be poured out of the little spout for testing. If the process in hand is not completed, the contents are washed back to the bulk, and the operation repeated as often as may be required.

THE CALIBRATION OF GRADUATED APPARATUS.

It is obvious that in the practice of volumetric analysis the absolute correctness of the graduations of the vessels used to a given standard is not necessary so long as they agree with one another. In the present day there are many makers of instruments, some using the litre of 1000 grams of distilled water at 4° C., others at 15·5° C., and others again at 17·5° C. In these circumstances it is conceivable that operators may purchase, from time to time, a mixture of instruments of a heterogeneous character. The German Imperial Standard Commission have now made it legal only to use for official purposes the litre and its divisions, containing 1000 grams of pure water at 4° C. (p. 23). These instruments for use in that country are all stamped in the same way as commercial measures are stamped by law in this country. If, then, instruments are sent abroad, they will not agree with the bulk of those hitherto used. On this account, as well as for general accuracy, it is necessary to calibrate or measure the divisions upon the various instruments by actual experiment, carried on in a room kept at the temperature of 15° C.

Flasks.—The shortest way to get at the true contents of a litre flask, or to correct it for a given temperature by making a fresh mark, is to weigh the contents by substitution, which is done as follows :—

The flask is cleaned and dried, by first rinsing with alcohol, then ether, and the latter blown out with a bellows or driven off by warming. When cool, it is placed on a sufficiently large and sensitive balance, together with a kilogram weight, side by side—a shallow metal tray is placed on the other pan, and sufficient shot added to exactly balance the flask and weight ; both the latter are then removed, leaving the shot on the other pan. The flask is then placed level, and distilled water at 15° C. poured in up to the mark ; the moisture in the neck is removed after a few minutes by filter paper and the flask placed on the empty pan. If the two pans are in equilibrium the mark is correct ; if not, water must be added or removed with a small pipette, and the mark altered. Smaller flasks are calibrated in the same way.

To calibrate a flask for *delivering* an exact litre or less, some water is poured into the empty flask, which is drained for half a minute, and weighed with its stopper ; it is then filled to the neck with pure water, and closed by the glass or rubber stopper, to prevent evaporation, and water added or removed as before. A nick is then made with a diamond, or sharp file, opposite the lowest part of the meniscus, which may be extended to a proper mark after the flask is emptied. Such a flask, when correctly marked, will deliver the volume required at the given temperature, after the contents have been poured out and drained for half a minute.

Burettes.—After firmly fixing in its stand, filling with pure water at 15° C., and getting rid of the air bubbles in the tap or jet, the exact level at the 0 mark is made preferably with an Erdmann float ; successive quantities of 5 or 10 c.c. are then run into a small dry tared beaker and rapidly weighed. If great accuracy is required a closed vessel ought to be employed, but this necessitates the drying after each weighing ; a very small beaker can be easily wiped dry, and rapid weighings made without any sensible loss of accuracy. If the weighings have shown reasonable accuracy, say within a milligram or so for each c.c., it will be sufficiently correct ; if otherwise, a table must be constructed showing the correct contents at any given point.

An excellent method of calibrating tap burettes is described by Carnegie,* which saves the labour involved in the separate weighings just described, but does not give the weight contents. A small column of CS_2, saturated with water, and tinted with iodine, is used to measure the spaces between the graduation marks of the instrument. The burette is connected by rubber tube with a reservoir of water like that used for mercury in gas apparatus, and by the pressure of the water in this reservoir 5 c.c. or so of the CS_2 may be moved from the bottom upwards, throughout the whole length of the instrument, so as to compare portions of the scale throughout. It is essential that the measurement takes place from the bottom, which is done by allowing water to flow in up to the lower mark of the burette, then gently running in the portion of CS_2 from a long fine pipette ; when settled, and the meniscus observed, a cautious opening of the tap will allow of the movement of the column, through the various divisions, up to the top.

Pipettes.—With the instrument made to deliver one quantity only it is generally sufficient to fill it by suction above the mark, then gently release the pressure of the finger until the exact mark is reached. The contents are then run into a dry tared beaker, drained for 15 seconds in contact with the sides of the beaker, and the beaker quickly weighed. If not fairly correct, trials must be made by placing a thin strip of gummed paper on the stem, and marking

* *C. N.* **64**, 42.

the height of each trial until the correct weight is found, when a permanent mark may be made.

Graduated pipettes are best calibrated by filling them above the mark, fixing them in a stand like a burette, closing the top with a stout piece of rubber tube, clamped with a strong clip, then, after adjusting the level, drawing off in quantities of 5 c.c. or so, and weighing in the same way as directed for burettes.

Cylinders.—The only method of calibrating these vessels is to measure into them repeatedly various volumes of water from delivery pipettes of proved accuracy, taking precautions as to level, meniscus, and the proper drainage of the pipette after each delivery.*

Preservation of Solutions.—There are test solutions which, in consequence of their proneness to decomposition, cannot be kept at

Fig. 24.

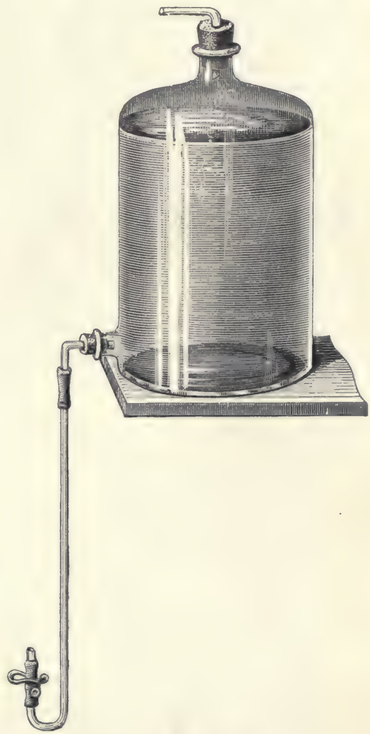


Fig. 25.

any particular strength for a length of time ; consequently they must be titrated on every occasion before being used. Stannous chloride and sulphurous acid are examples of such solutions. Special vessels

* An excellent method of calibration for volumetric instruments is given by Morse and Blalock (*Amer. Chem. Journ.* **16**, 479).

have been devised for keeping solutions liable to alter in strength by access of air, as shown in figs. 24 and 25.

Fig. 24 is especially applicable to caustic alkali solutions, the tube passing through the caoutchouc stopper being filled with dry soda-lime, resting on cotton wool.

Fig. 25, designed by Mohr, is a considerable improvement upon this, since it allows of the burette being filled with the solution from the store bottle quietly, and without any access of air whatever. The vessel can be used for caustic alkalies, baryta, stannous chloride, permanganate, and sulphurous acid, or any other liquid liable to undergo change by absorbing oxygen. Rubber stoppers should be used for these bottles ; and a thin layer of white mineral oil is poured on the top of the solution, where, owing to its low density, it always floats, placing an impermeable division between the air and the solution ; and as this oil is not affected by these solutions in their diluted state, this form is of great advantage. Fig. 25 can be improved by having a two-holed rubber stopper—one hole is used for a tapped funnel, through which the bottle is filled, the other hole contains a small tapped tube, which is opened when drawing the solution out or when filling the bottle. Solutions not affected chemically by contact with air should be kept in bottles, the corks or stoppers of which keep them perfectly closed, and tied over with india-rubber or bladder to prevent evaporation, and should further be always shaken before use, when they are not quite full. The influence of bright light upon some solutions is very detrimental to their chemical stability ; hence it is advisable to preserve some solutions not in immediate use in the dark, and at a temperature not exceeding 15 or 16° C.

The apparatus devised by J. C. Chorley, and shown in fig. 26, will be found useful for preserving and delivering known volumes of such solutions as alcoholic potash, which are liable to alteration by exposure to air. The wash bottle inserted in the cork of the large store bottle contains a solution of caustic soda, and serves to wash all air entering the large bottle. By means of the three-way stop-cock at the bottom of the apparatus the solution is allowed to fill the pipette and overflow into its upper chamber, the excess being caught in the small side bulb and reservoir ; this solution serves to wash all air entering the pipette when the stop-cock is turned to deliver the solution, which is run off to a mark just above the tap. When full, the side reservoir may be emptied by withdrawing the small ground stopper.

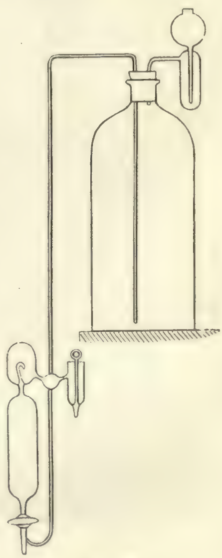


Fig. 26.

ON THE SYSTEM OF WEIGHTS AND MEASURES TO BE ADOPTED IN VOLUMETRIC ANALYSIS.*

It is much to be regretted that the metric system of weights and measures used on the Continent is not universally adopted, for both scientific and general purposes, throughout the civilized world. The two great advantages of the metric system are that it is, first, a decimal system and, secondly, a simply-related system. A short description of the origin and development of this system may not here be out of place.

The Metric System is founded on the *metre*, which was originally intended to be one-ten-millionth part of a quadrant of the meridian through Paris, in other words, one forty-millionth part of the circumference of the earth. Subsequent measurements, however, have shown that the metre does not exactly represent this, hence the unit becomes an arbitrary measure after all.

All the multiples of units in the Metric System are indicated by Greek prefixes, all fractions or submultiples by Latin prefixes, thus :—

kilo = a thousand times	milli = a thousandth part, or ·001
hecto = a hundred times	centi = a hundredth part, or ·01
deca = ten times	deci = a tenth part, or ·1
the unit to which it is prefixed.	of the unit to which it is prefixed.

For example, a hectogram = 100 grams
a millimetre = one-thousandth part of a metre, or ·001 metre.

The decimals of a metre are abbreviated thus :—

Millimetre,s = mm.
Centimetre,s = cm.
Decimetre,s = dm.

The unit of surface is the *are*, which is a square whose side is 10 metres. Consequently it equals 100 square metres and is indicated thus :—1 are = 100 m^2.

The unit of volume is a cube whose side measures one decimetre and it is called the litre.

1 litre = 1 cubic decimetre (or dm^3.)
= 1000 cubic centimetres (c.c., c.cm., or cm^3.).

The standard of weight (strictly speaking, of *mass*) in the metric system is the kilogram, which was constructed to represent the weight of a cubic decimetre of pure distilled water at its point of maximum density, reckoned at 4° C. In this way a most intimate and useful relationship between volumes and weights is obtained. Thus, at 4° C., a cubic decimetre of water weighs 1000 grams and conversely 1000 grams of water occupy 1 litre. Similarly a litre

* The author is greatly indebted to Dr. R. T. Glazebrook, F.R.S., Director of the National Physical Laboratory, for kindly supplying data used both in this section and in those dealing with the pipette and the measuring flask.

of alcohol of sp. gr. 0·9198 at 4° C. weighs $1000 \times \cdot 9198 = 919\cdot 8$ grams. For scientific purposes the kilogram is usually too large a unit, hence for practical use the weight made use of is the gram and its subdivisions.

Further investigations having shown that the above relations do not strictly hold good, the litre is now defined as follows :—

The standard litre is the volume of a kilogram of pure water at 4° C.

The value of the litre in terms of the cubic centimetre has been the subject of numerous experiments. The best determination gives :—

1 litre = 1000·028 cubic centimetres.

This is based on very exact measurements made during the last few years, as follows :—

Method.	Experimenter.	Result.
Mechanical contact	Guillaume	1000·029
Interference by reflection	Chappuis	1000·027
,, ,, transmission	Macé de Lepinay Benôit Buisson	1000·028

Hence, one decilitre = 100·0028 cubic centimetres
one millilitre = 1·000028 ,, ,,

Thus the difference between the two is practically negligible, and in all but the most refined experiments the volume of one cubic centimetre may be treated as one-thousandth part of that of the litre. Now since in chemical laboratories it is not customary to work at a temperature of 4° C., Mohr introduced another standard, known as Mohr's litre, which is the volume occupied by 1000 grams of water at the temperature of 16° C., this being considered about the average temperature of a working laboratory. On this system the cubic centimetre should contain 1 gram of distilled water at 16° C., and a 10 c.c. pipette, for example, should deliver 10 grams of distilled water at 16° C. 1000 true c.c. contain almost exactly 999 grams of water at 16° C.

From these considerations it becomes evident that it is of the first importance to the analyst that he takes care to work with a complete set of volumetric measures all graduated on one plan *or* the other.

Measures marked, e.g., "25 c.c. 15° C" should contain or deliver, as the case may be, 25 true c.c. when the instrument is at the temperature of 15° C. On the other hand, a flask marked "1000 grams 16° C." should, of course, contain 1000 grams of distilled water at the temperature of 16° C., i.e., a Mohr's litre. Vessels graduated according to Mohr's system should bear the word "Gramme" or the letters "Grm" together with the temperature. It should be noted that the German Kaiserliche Normal-Eichungs Kommission no longer employs Mohr's unit.

The usual standard temperature for volumetric vessels is 15° C., which means that a vessel contains its nominal content of water when the vessel is at 15° C. This is usually judged by the water being steady at 15° C., and for exactness the surrounding air should be at 15° C. also. When the vessel is at a different temperature, its volume alters in accordance with the coefficient of cubical expansion of the glass. Various other temperatures in addition to the standard 15° C. are, however, in common use, as for instance 20° C. for vessels employed in connection with polarimeters or viscosimeters, 80° or 82° F. for vessels intended for tropical climates, and so on.

The British equivalents of the principal metric units are as follows :—

1 metre	=	39·370113 inches.
1 are	=	119·59921 square yards.
1 litre	=	1·75980 pints.
	=	0·219975 gallons.
1 kilogram	=	2·2046223 lb. avoirdupois.
1 gram	=	15·43236 grains.

Variations of Temperature.—In the preparation of standard solutions one thing must especially be borne in mind, namely, that saline substances on being dissolved in water have a considerable effect upon the volume of the resulting liquid. The same is also the case in mixing solutions of various salts or acids with each other.*

In the preparation of strong solutions the contraction in volume is as a rule considerable. Hence, in preparing such solutions for volumetric analysis, or in diluting such solutions to a given volume for the purpose of removing aliquot portions subsequently for examination, sufficient time must be given for liquids to acquire their constant volume at the standard temperature. If the strength of a standard solution is known for one temperature, the strength corresponding to another temperature can only be calculated if the rate of expansion by heat of the liquid is known. The variation cannot be estimated by the known rule of expansion of distilled water ; for Gerlach has shown that even weak solutions of acids and salts expand far more than water for certain increments of temperature. The rate of expansion for pure water is known, and may be used for the purpose of verifying the graduation of instruments where extreme accuracy is required. The following short table furnishes the data for correction.

The weight of 1000 c.c. of water at t° C., when determined by means of brass weights in air of t° C., and at 760 m.m. pressure is equal to $1000-x$ gm.

Slight variations of atmospheric pressure may be entirely disregarded.

* See Gerlach, "Specifische Gewichte der Salzlösungen;" also Gerlach, "Sp. Gewichte von wässerigen Lösungen," *Z. a. C.* **8**, 245.

$t°$	10	11	12	13	14	15	16	17	18	19	
x	1·34	1·43	1·52	1·63	1·76	1·89	2·04	2·2	2·37	2·55	
$t°$	20	21	22	23	24	25	26	27	28	29	30
x	2·74	2·95	3·17	3·39	3·63	3·88	4·13	4·39	4·67	4·94	5·24

x is the quantity to be subtracted from 1000 to obtain the weight of 1000 c.c. of water at the temperature $t°$. Thus at 20° 2·74 must be deducted from 1000 = 997·26.

Bearing the foregoing remarks in mind, therefore, the safest plan in the operations of volumetric analysis, so far as measurement is concerned, is to use solutions as dilute as possible. Absolute accuracy in determining the strength of standard solutions can only be secured by the process of weighing, the ratio of the weight of the solution to the weight of active substance in it being independent of temperature.

Casamajor* has made use of the data given by Matthiessen in his researches on the expansion of glass, water, and mercury, to construct a table of corrections to be used when using any weak standard solution at a different temperature from that at which it was originally standardized.

The expansion of water is different at different temperatures; the expansion of glass is known to be constant for all temperatures up to 100° C. The correction of volume, therefore, in glass burettes must be the known expansion of each c.c. of water for every 1° C., less the known expansion of glass for the same temperature.

It is not necessary here to reproduce the entire paper of Casamajor, but the results are shortly given in the following table.

The normal temperature is 15° C.; and the figures given are the relative contractions below, and expansions above, 15° C

Deg. C.		Deg. C.	
7	−·000612	24	+·001686
8	−·000590	25	+·001919
9	−·000550	26	+·002159
10	−·000492	27	+·002405
11	−·000420	28	+·002657
12	−·000334	29	+·002913
13	−·000236	30	+·003179
14	−·000124	31	+·003453
15	Normal	32	+·003739
16	+·000147	33	+·004035
17	+·000305	34	+·004342
18	+·000473	35	+·004660
19	+·000652	36	+·004987
20	+·000841	37	+·005323
21	+·001039	38	+·005667
22	+·001246	39	+·006040
23	+·001462	40	+·006382

* *C. N.* **35**, 160.

By means of these numbers it is easy to calculate the volume of liquid at 15° C. corresponding to any volume observed at any temperature. If 35 c.c. of solution has been used at 37° C., the table shows that 1 c.c. of water in passing from 15° to 37° is increased to 1·005323 c.c.; therefore, by dividing 35 c.c. by 1·005323 is obtained the quotient 34·819 c.c., which represents the volume at 15° corresponding to 35 c.c. at 37°. The operation can be simplified by obtaining the factor, thus:

$$\frac{1}{1{\cdot}005323}=0{\cdot}994705$$

and $35 \times 0{\cdot}9947 = 34{\cdot}82$

A table can thus be easily constructed which would show the factor for each degree of temperature.

These corrections are useless for concentrated solutions, such as normal alkalies or acids; with great variations of temperature these solutions should be used by weight.

Instruments graduated on the Grain System.—Burettes, pipettes, and flasks may also be graduated in grains, in which case it is best to take 10,000 grains as the standard of measurement. In order to lessen the number of figures used in the grain system, so far as liquid measures are concerned, I propose that ten fluid grains be called a decem, or for shortness dm. This term corresponds to the cubic centimetre, bearing the same proportion to the 10,000 grain measure as the cubic centimetre does to the litre, namely, the one-thousandth part. The use of a term like this will serve to reduce the number of figures which are unavoidably introduced by the use of a small unit like the grain.

Its utility is principally apparent in the analysis for percentages, particulars of which will be found hereafter.

The 1000 grain burette or pipette will therefore contain 100 decems, the 10,000 gr. measure 1000 dm., and so on.

The capacities of the various instruments graduated on the grain system may be as follows:—

Flasks: 10,000, 5000, 2500, and 1000 grs. = 1000, 500, 250, and 100 dm. Burettes: 300 grs. in 1-gr. divisions, for very delicate purposes = 30 dm. in $\frac{1}{10}$; 600 grains in 2-gr. divisions, or $\frac{1}{5}$ dm.; 1100 grs. in 5-gr. divisions, or $\frac{1}{2}$ dm.; 1100 grs. in 10-gr. divisions, or 1 dm. The burettes are graduated above the 500 or 1000 grs. in order to allow of analysis for percentages by the residual method. Whole pipettes to deliver 10, 20, 50, 100, 200, 500, and 1000 grs.; graduated ditto, 100 grs. in $\frac{1}{10}$ dm.; 500 grs. in $\frac{1}{2}$ dm.; 1000 grs. in 1 dm.

Those who may desire to use the decimal systems constructed on the gallon measure (= 70,000 grains) will bear in mind that the "septem" of Griffin, or the "decimillem" of Acland are each equal to 7 grs.; and therefore bear the same relation to the pound (= 7000 grs.) as the cubic centimetre does to the litre, or the

decem to 10,000 grs. An entirely different set of tables for calculations, etc., is required for these systems; but the analyst may readily construct them when once the principles contained in this treatise are understood.

VOLUMETRIC ANALYSIS BASED ON THE SYSTEM OF CHEMICAL EQUIVALENCE AND THE PREPARATION OF NORMAL TITRATING SOLUTIONS.

WHEN analysis by measure first came into use, the test solutions were generally prepared so that each substance to be tested had its own special reagent; and the strength of the standard solution was so calculated as to give the result in percentages. Consequently, in alkalimetry, a distinct standard acid was used for soda, another for potash, a third for ammonia, and so on, necessitating a great variety of standard solutions.

Griffin and Ure appear to have been the first to suggest the use of standard test solutions based on the atomic system; and following in their steps Mohr has worked out and verified many methods of analysis which are of great value to all who concern themselves with scientific and especially with technical chemistry. Not only has Mohr done this, but he has enriched his processes with so many original investigations, and improved the necessary apparatus to such an extent, that he may with justice be called the father of the volumetric system.

Normal Solutions.—It is of great importance that no misconception should exist as to what is meant by a normal solution; but it does unfortunately occur, as may be seen by reference to the chemical journals, also to Muir's translations of Fleischer's book.*

Normal solutions may be defined as follows:—

A normal solution of a reagent is one that contains in a litre that proportion of its molecular weight in grams which corresponds to one gram of available hydrogen or its equivalent.

Seminormal, quintinormal, decinormal and centinormal solutions are also required and are shortly designated as $^N/_2$ $^N/_5$ $^N/_{10}$ and $^N/_{100}$ solutions.†

* See Allen, *C. N.* **40**, 239, also *Analyst*, **13**, 181.

† It is much to be regretted that the word "normal," originally based on the equivalent system, should now be appropriated by those who advocate the use of solutions based on molecular weights, because it not only leads to confusion between the two systems, but to utter confusion between the advocates of the change themselves. In Fleischer's German edition of his *Maasanalyse* the molecular system is advocated, but, as the old atomic weights are used, the solutions are really, in the main, of the same strength as those based on the equivalent system. Pattinson Muir, however, in his translation, has thought proper to use modern atomic weights, and the curious result is that one is directed to prepare a normal solution of caustic potash, with 39·1 grams K to the litre, while a normal potassium carbonate is to contain 138·2 grams K_2CO_3, or 78·2 grams K, in the same volume of solution. Again, Muter, in his *Manual of Analytical Chemistry*, defines a normal solution as having one molecular weight of the reagent in grams per litre; then follows the glaring inconsistency, among others, of directing that a decinormal solution of iodine should contain 12·7 grams of I per litre, whereas, if it was made strictly according to the original definition, it should contain 25·4 grams in the litre. Menschutkin's *Analytical*

Thus, a normal solution of hydrochloric acid contains 36·47 grams in a litre, because this weight of the acid contains one gram of hydrogen; similarly normal sodium hydroxide contains 40·01 grams per litre. Oxalic acid contains in the molecule two atoms of hydrogen, both available, and consequently normal oxalic acid contains $\frac{126 \cdot 06}{2} = 63 \cdot 03$ grams of the crystallized acid ($H_2C_2O_4 2H_2O$) in the litre. Similarly, a normal solution of sodium phosphate would be made by dissolving one-third of the molecular weight of the crystallized salt, in grams, in water and diluting the solution to 1 litre, because orthophosphoric acid contains 3 atoms of available hydrogen in its molecule.

In preparing a normal solution of potassium permanganate for use as an oxidizing agent we know that $K_2Mn_2O_8$ gives up 5 atoms of available oxygen, equivalent to 10 atoms of available hydrogen. Hence, a normal solution of potassium permanganate contains $\frac{316 \cdot 06}{10} = 31 \cdot 606$ grams of the crystallized salt per litre.

Normal alkali solutions are always such that a given volume requires for neutralization an equal volume of a normal acid solution.

Other instances will be given later on and explained in detail in their proper place.

A further illustration may be given in order to show the method of calculating the results of this kind of analysis.

Each c.c. of $^{N}/_{10}$ silver nitrate solution will contain $\frac{1}{10000}$ of the atomic weight of silver $= 0 \cdot 010788$ gm., and will exactly precipitate $\frac{1}{10000}$ of the atomic weight of chlorine $= 0 \cdot 003546$ gm. from any solution of a chloride.

In the case of normal oxalic acid each c.c. will contain $\frac{1}{2000}$ of the molecular weight of the crystallized acid $= 0 \cdot 06303$ gm., and will neutralize $\frac{1}{2000}$ of the molecular weight of sodium carbonate $= 0 \cdot 053$ gm., or will combine with $\frac{1}{2000}$ of the atomic weight of a dyad metal such as lead $= 0 \cdot 10355$ gm., or will exactly saturate $\frac{1}{1000}$ of the molecular weight of sodium hydrate $= 0 \cdot 040$ gm., and so on.

Where the 1000 grain measure is used as the standard in place of the litre, 63·03 grains of oxalic acid would be used for the normal solution; but as 1000 grains is too small a quantity to make, it is better to weigh 630 grains, and make up the solution to 10,000 grain

Chemistry, translated by Locke, recently published by Macmillan and Co., unfortunately adopts the molecular system.

If the unit H be adopted as the basis or standard, everything is simplified, and actual normal solutions may be made and used; but, on the molecular system, this is, in many cases, not only unadvisable but impossible, besides leading to ridiculous inconsistencies. As Allen points out in the reference above, it is, to say the least of it, highly inconvenient that the nomenclature of a standard solution should be capable of two interpretations. I have given the term *systematic* to this handbook, and I maintain that the equivalent system used is the only systematic and consistent one; it was adopted originally by Mohr, followed by Fresenius, and continued by Classen in the new edition of Mohr's *Titrirmethode*. Allen himself has unhesitatingly preferred to use it in his *Organic Analysis*, and these, together with this treatise, being all text-books having a wide circulation, ought to settle definitely the meaning of the term *normal* as applied to systematic standard solutions. Anyhow, it is to be hoped that those who communicate processes to the chemical journals, or abstracters of foreign articles for publication, will take care to distinguish between the conflicting systems.

measure (=1000 dm.). The solution would then have exactly the same strength as if prepared on the litre system, as it is proportionately the same in chemical value; and either solution may be used indiscriminately for instruments graduated on either scale, bearing in mind that the substance to be tested with a burette graduated in c.c. must be weighed on the gram system, and *vice versâ*, unless it be desired to calculate one system of weights into the other.

The great convenience of this equivalent system is that the numbers used as coefficients for calculation in any analysis are familiar, and the solutions agree with each other, volume for volume. We have, hitherto, however, looked only at one side of its advantages. For technical purposes the plan allows the use of all solutions of systematic strength, and simply varies the amount of substance tested according to its equivalent weight.

Thus, the normal solutions say, are—

Crystallized oxalic acid	**=63·03 gm.**	**per litre**
Sulphuric acid	**=49·043 gm.**	,,
Hydrochloric acid	**=36·47 gm.**	,,
Nitric acid	**=63·02 gm.**	,,
Anhydrous sodium carbonate	**=53 gm.**	,,
Sodium hydroxide	**=40·01 gm.**	,,
Ammonia	**=17·034 gm.**	,,

100 c.c. of any one of these normal acids should exactly neutralize 100 c.c. of any of the normal alkalies, or the corresponding amount of pure substance which the 100 c.c. contain. In commerce we continually meet with substances used in manufactures which are not pure, and it is necessary to know how much pure substance they contain.

Take, for instance, refined soda ash (sodium carbonate). If it were absolutely pure, 5·3 gm. of it should require exactly 100 c.c. of any normal acid to saturate it. If we therefore weigh that quantity, dissolve it in water, and deliver into the mixture the normal acid from a burette, the number of c.c. required to saturate it will show the percentage of pure sodium carbonate in the sample. Suppose 90 c.c. are required=90 %.

Again—a manufacturer buys common oil of vitriol, and requires to know the exact percentage of pure hydrated acid in it; 4·9 grams are weighed, diluted with water, and normal alkali delivered in from a burette till saturated; the number of c.c. used will be the percentage of real acid. Suppose 58·5 c.c. are required=58·5 %.

On the grain system, in the same way, 53 grains of the sample of soda ash would require 90 dm. of normal acid, also equal to 90 %.

Or, suppose the analyst desires to know the equivalent percentage of sodium oxide, free and combined, contained in the above sample of soda ash, without calculating it from the carbonate found as above, 3·1 gm. is treated as before, and the number of c.c. required

is the percentage of sodium oxide. In the same sample 52·6 c.c. would be required = 52·6 per cent. of sodium oxide, or 90 per cent. of sodium carbonate.

Method for percentage of Purity in Commercial Substances.— The rules, therefore, for obtaining the percentage of pure substances in any commercial article, such as alkalies, acids, and various salts, by means of systematic normal solutions such as have been described are these—

1. With normal solutions $\frac{1}{10}$ or $\frac{1}{20}$ (according to its atomicity) of the molecular weight in grams of the substance to be analysed is to be weighed for titration, and the number of c.c. required to produce the desired reaction is the percentage of the substance whose atomic weight has been used.

With decinormal solutions $\frac{1}{100}$ or $\frac{1}{200}$ of the molecular weight in grams is taken, and the number of c.c. required will, in like manner, give the percentage.

Where the grain system is used it will be necessary, in the case of titrating with a normal solution, to weigh the whole or half the molecular weight of the substance in grains, and the number of decems required will be the percentage.

With decinormal solutions, $\frac{1}{10}$ or $\frac{1}{20}$ of the molecular weight in grains is taken, and the number of decems will be the percentage.

It now only remains to say, with respect to the system of weights and measures to be used, that the analyst is at liberty to choose his own plan. Both systems are susceptible of equal accuracy, and he must study his own convenience as to which he will adopt. The normal solutions prepared on the gram system are equally applicable for that of the grain, and *vice versâ*, so that there is no necessity for having distinct solutions for each system

Factors, or Coefficients, for the Calculation of Analyses.—It frequently occurs that from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed. For instance, suppose the operator has a solution containing an unknown quantity of caustic potash, the strength of which he desires to know ; a weighed or measured quantity of it is brought under the normal acid burette and exactly saturated, 32 c.c. being required. The calculation is as follows :—

The molecular weight of potassium hydroxide being 56·11 : 100 c.c. of normal acid will saturate 5·611 gm. ; therefore, as 100 c.c. are to 5·611 gm., so are 32 c.c. to x, $\frac{5{\cdot}611 \times 32}{100} = 1{\cdot}796$ gm. KHO.

The simplest way, therefore, to proceed, is to multiply the number of c.c. of test solution required in any analysis by the $\frac{1}{1000}$ (or $\frac{2}{1000}$ if bivalent) of the molecular weight of the substance sought, which gives at once the amount of substance present.

An example may be given—1 gm. of marble or limestone is taken for the determination of pure calcium carbonate, and exactly

saturated with normal nitric or hydrochloric acid—(sulphuric or oxalic acid is, of course, not admissible) 17·5 c.c. are required, therefore $17 \cdot 5 \times 0 \cdot 050$ (the $\frac{1}{2000}$ of the molecular weight of $CaCO_3$) gives 0·875 gm. and as 1 gm. of substance only was taken = 87·5 % of calcium carbonate

ON THE DIRECT AND INDIRECT PROCESSES OF ANALYSIS AND THEIR TERMINATION.

THE direct method includes all those analyses where the substance under examination is decomposed by simple contact with a known quantity or equivalent proportion of some other body capable of combining with it, and where the end of the decomposition is manifest in the solution itself.

It also properly includes those analyses in which the substance reacts upon another body to the expulsion of a representative equivalent of the latter, which is then determined as a substitute for the thing required.

Examples of this method are readily found in the process for the determination of iron by permanganate, where the beautiful rose colour of the permanganate asserts itself as the end of the reaction.

The testing of acids and alkalies comes, also, under this class, the great sensitiveness of litmus, or other indicators, causing the most trifling excess of acid or alkali to alter their colour.

The *indirect method* is exemplified in the analysis of manganese ores, and also other peroxides and oxygen acids, by boiling with hydrochloric acid. The chlorine evolved is determined as the equivalent of the quantity of oxygen which has displaced it. We are indebted to Bunsen for a most accurate and valuable series of processes based on this principle.

The *residual method* is such that the substance to be analysed is not itself determined, but the excess of some other body added for the purpose of combining with it or of decomposing it; and the quantity or chemical value of the body added being known, and the conditions under which it enters into combination being also known, by deducting the remainder or excess (which exists free) from the original quantity, it gives at once the proportional quantity of the substance sought.

An example will make the principle obvious:—Suppose that a sample of native calcium or barium carbonate is to be titrated. It is not possible to determine it with standard nitric or hydrochloric acid in the exact quantity it requires for solution. There must be an excess of acid and heat applied also to get it dissolved; if, therefore, a known excessive quantity of standard acid be first added and solution obtained, and the liquid then titrated back with standard alkali and an indicator, the quantity of free acid can be exactly determined, and consequently that which is combined also.

In some analyses it is necessary to add a substance which shall be an indicator of the end of the process ; such, for instance, is litmus or the azo colours in alkalimetry, potassium chromate in silver and chlorine, and starch in iodine determinations.

There are other processes, the end of which can only be determined by an indicator separate from the solution ; such is the case in the determination of iron by potassium bichromate, where a drop of the liquid is brought into contact with another drop of solution of potassium ferricyanide on a white slab or plate ; when a blue colour ceases to form by contact of the two liquids, the end of the process is reached.

PART II.

ALKALIMETRY.

Gay Lussac based his system of alkalimetry upon a standard solution of sodium carbonate, with a corresponding solution of sulphuric acid. It possesses the recommendation that a pure standard solution of sodium carbonate can be more readily obtained than any other form of alkali. Mohr introduced the use of caustic alkali instead of a carbonate, the strength of which is established by a standard solution of oxalic or sulphuric acid. The advantage in the latter system is that in titrating acids with a caustic alkali the well-known interference produced in litmus by carbonic acid is avoided; this difficulty is now overcome wherever it is desired by the new indicators to be described.

INDICATORS USED IN ALKALIMETRY.

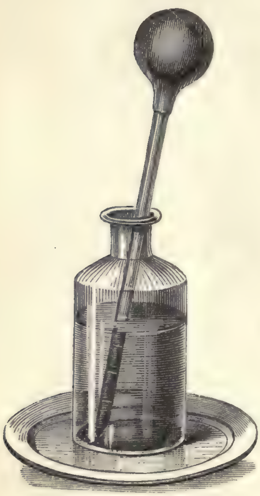


Fig. 27.

1. **Litmus Solution.**—It has been the custom since the introduction of the azo and other modern indicators to regard litmus as old fashioned and of very doubtful sensitiveness. This is a mistake, for if properly prepared it is, in the absence of carbonic acid, one of the most sensitive of the indicators used for alkalies. The litmus of commerce differs considerably in purity and colour, but a careful examination will at once detect a good specimen by the absence of a greyish muddy colour, due to inert matters, both of vegetable and mineral nature. The sensitive colouring matter in litmus is azolitmin, and by purifying ordinary litmus, as described below, some interfering bodies are removed, with the result that the indicator is far more sensitive.

A simple solution may be made by treating the cubes repeatedly with small quantities of hot water, mixing all the extracts, and allowing the liquid to stand in a covered beaker for a day or night. The clear blue liquid is then poured off and placed in the stock bottle, together with two or three drops of chloroform. This latter agent prevents the development of bacteria, and if the bottle is simply closed with a loose cork, through which the delivery pipette is passed, the solution will keep for a long period. If the colour is a deep blue it must be modified by a few drops of weak acid, until it is a faint

purple. In course of time it may lose its colour, but this may be restored by simple exposure to the air in a basin. Another method of preparing an extract of litmus in a concentrated form for dilution whenever required is as follows. Extract all soluble matters from the solid litmus by repeated treatment with hot water; evaporate the mixed extracts to a moderate bulk, and add acetic acid in slight excess to decompose carbonates; evaporate to a thick extract, transfer this to a beaker, and add a large proportion of hot 85 per cent. alcohol or methylated spirit. By this treatment the blue colour is precipitated, and the alkaline acetates, together with some red colouring matter, remain dissolved; the fluid with precipitate is thrown on a filter, washed with hot spirit, and the purified extract finally evaporated to a paste, which is placed in a wide-mouthed bottle. This extract will keep for years unchanged.

Another method also gives good results. The crushed litmus is extracted with warm distilled water, as before described, and the several extracts mixed, then allowed to stand in a beaker till quite clear. This clear extract is poured off, strongly acidified with hydrochloric acid, and put in a dialyser, which is surrounded by running water and kept so for about a week. The colouring matter of litmus being a colloid, all the calcium and other salts are removed, and a pure colour soluble in hot distilled water remains, which may be preserved in the manner previously described, or evaporated to a soft extract.

A sensitive and stable solution of litmus is said to be prepared as follows:—

100 gm. of commercial litmus are extracted with successive quantities of hot water until the united extracts measure 600 c.c. The extract is then allowed to settle, preferably at a low temperature, and the clear solution is decanted and evaporated to about 200 c.c. After filtration, the solution is diluted with water to 300 c.c., 100 c.c. of 16 per cent. sulphuric acid are added, and the mixture is heated on a water-bath for 4 hours. The flocculent precipitate formed is separated by filtration and washed with cold water until all sulphuric acid has been removed and the faintly red wash-water becomes bright blue when rendered alkaline. The precipitate on the filter is then dissolved in about 100 c.c. of hot alcohol, which is used in small quantities at a time; a few drops of ammonia may be added to the later quantities of alcohol. The alcoholic solution is now evaporated to dryness, the residue dissolved in 600 c.c. of hot water, and the solution neutralized with potash.

Free carbonic acid interferes considerably with the production of the blue colour, and its interference in titrating acid solutions with alkali carbonates can only be got rid of by boiling the liquid during the operation, in order to dispel the gas. If this is not done, it is easy to overstep the exact point of neutrality in endeavouring to produce the blue colour. The same difficulty is also found in obtaining the pink-red when acids are used for titrating alkali carbonates, hence the value of the caustic alkali solutions free from carbonic acid when this indicator is used.

It sometimes occurs that titration by litmus is required at night.

* A. Puschel, Oesterr. Chem.-Zeit., 1910, 13, 185.

Ordinary gas or lamp light is not adapted for showing the reaction in a satisfactory manner ; but a very sharp line of demarcation between red and blue may be found by using a monochromatic light. With the yellow sodium flame the red colour appears perfectly colourless, while the blue or violet appears like a mixture of black ink and water. The transition is very sudden, and even sharper than the change by daylight.

The operation should be conducted in a perfectly dark room ; and the flame may be obtained by heating a coiled platinum wire sprinkled with salt, or a piece of pumice saturated with a concentrated solution of salt, in the Bunsen flame, or by means of one of the sodium lamps now on the market.

According to R. Reinitzer* litmus solution is the most serviceable indicator, excelling methyl orange in sharpness of change of colour and sensitiveness (about 8 times as great) while it possesses an advantage over phenolphthalein in being capable of being used in the presence of ammonium salts. The final change of colour is sharpest when the liquid to be titrated is boiled for seven or eight minutes and then well cooled. In order to avoid the influence of atmospheric carbonic acid it should not be allowed to stand exposed for long, and dilution with unboiled distilled water should be avoided. It is important to note that the liquid must be cold when titrated. Lunge† admits that litmus, when prepared and used according to Reinitzer's directions, is more sensitive than methyl orange, but found it to be only twice as sensitive. With normal acid practically identical results are obtained, but methyl orange is preferable on account of its speed and the precautions to be observed in the use of litmus. With semi-normal acid the change of colour is more difficult to observe in the case of methyl orange, but a practised observer can be sure to a drop. It is only with $^{N}/_{10}$ acid that litmus is undoubtedly superior, and Reinitzer's method of titration must be observed.

2. **Litmus Paper.**—Is made by dipping strips of calendered unsized paper in the solution and drying them ; the solution used being rendered blue, red, or violet as may be required.

3. **Cochineal Solution.**—This indicator possesses the advantage over litmus that it is not so much modified in colour by the presence of carbonic acid and may be used by gas-light. It may also be used with the best effect with solutions of the alkaline earths, such as lime and baryta water ; the colour with pure alkalies and earths is especially sharp and brilliant. The solution is made by digesting 1 part of crushed cochineal with 10 parts of 25 per cent. alcohol. Its natural colour is yellowish-red, which is turned to violet by alkalies ; mineral acids restore the original colour. It is not so easily affected by weak organic acids as litmus, and therefore for these acids the latter is preferable. It cannot be used in the presence of even traces of iron or alumina compounds or acetates, which fact limits its use. Carminic acid is the true sensitive element in cochineal, and it is sometimes preferable to cochineal in very delicate operations.

4. **Turmeric Paper.**—Pettenkofer, in his determination of carbonic acid by baryta water, prefers turmeric paper as an indicator. For this purpose it is best prepared by digesting pieces

* See *The Analyst*, 1894, p. 255. † *Ibid*, 1895, p. 65.

of the root, first in repeated small quantities of water to remove a portion of objectionable colouring matter, then in alcohol, and dipping strips of calendered unsized paper into the alcoholic solution, drying and preserving them in the dark. Or one part of powdered turmeric may be digested for about an hour with six parts of weak alcohol (3 volumes of alcohol to 1 of water) in a covered flask, with occasional shaking. The filtered liquid (tincture of turmeric) is used to prepare turmeric paper. Both liquid and paper should be protected from light.

Thomson, in continuance of his valuable experiments on various indicators, found that turmeric paper is of very little use for ammonia, or the alkali carbonates, or sulphides or sulphites, but he prepared a special paper of a light red-brown colour by dipping it into tincture of turmeric rendered slightly alkaline by caustic soda. If this paper is wetted with water the colour is intensified to a dark red-brown ; when partly immersed in a very dilute solution of an acid, the wetted portion becomes bright yellow, while immediately above this a moistened dark red-brown band is formed and the upper dry portion retains its original colour. This appearance only occurs in the titration of a comparatively large proportion of an acid, when the latter is nearly all neutralized, and thus serves to indicate the near approach to the end-reaction. When neutral or alkaline, the colour of the immersed portion of paper is simply intensified as already described. This intensification is quite as decided as a change of tint. This red-brown paper is as sensitive as phenolphthalein for the titration of citric, acetic, tartaric, oxalic and other organic acids by standard soda or potash, and may be used for highly coloured solutions. It is also available, like phenolphthalein, for the determination of small quantities of acid in strong alcohol.

Indicators derived from the Azo Colours, etc.

A great stride has been taken in the application of these modern indicators, and the thanks of all chemists are due to R. T. Thomson for his valuable researches on them, read before the Chemical Section of the Philosophical Society of Glasgow, and published in their Transactions.* The experiments recorded in these papers are carefully carried out, and the truthfulness of their results has been verified by Lunge and other practical men as well as by myself.

Space will only permit here of a record of the results, fuller details being given in the publications to which reference has been made.

5. **Methyl Orange,** or sodium dimethylamido-azo-benzene-sulphonate, is prepared by the action of diazotized sulphanilic acid upon dimethylaniline, the commercial product being the sodium salt of the sulphonic acid thus produced. If carefully prepared from the

* Reprinted *C. N.* **47**, 123, 185 ; **49**, 32, 119 ; *J. S. C. I.* **6**, 195.

purest materials it possesses a bright orange-red colour, and is perfectly soluble in water ; but the commercial product is often of a dull colour, due to slight impurities in the substances from which it is produced, and not completely soluble in water. These impurities may generally be removed by recrystallization from hot alcoholic solution. Complaints have been made by some operators that the commercial article is sometimes unreliable as an indicator ; it may be so, but, although I have examined many specimens, I have not yet found any in which the impurities sensibly affected its delicate action when used in the proper manner. The common error is the use of too much of it ; again, there is the personal error of observation, some eyes being much more sensitive to the change of tint than others. The great value of this indicator is that, unlike litmus and some other agents, it is comparatively unaffected by carbonic acid, sulphuretted hydrogen, hydrocyanic, silicic, boric, arsenious, oleic, stearic, palmitic, carbolic acids, etc. It must not be used for the organic acids, such as oxalic, acetic, citric, tartaric, etc., since the end-reaction is indefinite ; nor can it be used in the presence of nitrous acid or nitrites, which decompose it.* It may safely be used for the determination of free mineral acids in alum, ferrous sulphate or chloride, zinc sulphate, cupric sulphate or chloride. The acid radical (and consequently its equivalent metal) in cupric sulphate and similar salts may be determined with accuracy by precipitating the solution with sulphuretted hydrogen, filtering, and titrating the filtrate at once with normal alkali and methyl orange.

Methyl orange is especially useful for the accurate standardizing of any of the mineral acids by means of pure sodium carbonate in the cold, the liberated carbonic acid having practically no effect, as is the case with many indicators. Its effect is also excellent with ammonia or its salts. A convenient strength for the indicator is 1 gram of the powder in a litre of distilled water ; a single drop of the liquid is sufficient for 100 c.c. of any colourless solution—the colour being faint yellow if alkaline, and pink if acid ; if too much is used the end-reaction is slower and much less definite. All titrations with methyl orange should be carried on at ordinary temperatures if the utmost accuracy is desired, and the liquid titrated should not be too dilute Ethyl orange is similar to the methyl orange, but is not quite so sensitive.

6. **Phenacetolin.**—This indicator is slightly soluble in water but readily in 50 per cent. alcohol, and a convenient strength is 2 gm. per litre. The solution is greenish brown, giving a scarcely perceptible yellow with caustic soda or potash when a few drops are used with ordinary volumes of liquid. With ammonia and

* Some operators have used methyl orange in the titration of *alkaloids*, but in a series of very careful experiments, carried out by L. F. Kebler, it was found in some cases very defective (*Jour. Am. Chem. Soc.* Oct., 1895). Probably the most useful indicator for alkaloids is *Brazilin*, or a decoction of Brazil-wood; inapplicable in the presence of sulphuretted hydrogen or sulphurous acid.

the normal alkali carbonates it gives a dark pink, with bicarbonate a much more intense pink, and with mineral acids a golden yellow. This indicator may be used to determine the amount of caustic potash or soda in the presence of their normal carbonates if the proportion of the former is not very small, or of caustic lime in the presence of carbonate, but no ammonia must be present.

Practice, however, is required with solutions of known composition, so as to acquire knowledge of the exact shades of colour.

7. **Phenolphthalein** ($C_{20}H_{14}O_4$).—This indicator is of a resinous nature, but quite soluble in 50 per cent. alcohol. A convenient strength is 5 gm. per litre.

A few drops of the indicator show no colour in ordinary volumes of neutral or acid liquids; the faintest excess of caustic alkalies, on the other hand, gives a sudden change to purple-red.

This indicator is useless for the titration of free ammonia or its compounds, or for the fixed alkalies when salts of ammonia are present; except with alcoholic solutions, in which case caustic soda and potash displace the ammonia in equivalent quantities at ordinary temperatures, and the indicator forms no compound with the ammonia.

It may, however, be used like phenacetolin for determining the proportions of hydrate and carbonate of soda or potash in the same sample where the proportion of hydrate is not too small. Unlike methyl orange, this indicator is especially useful in titrating all varieties of organic acids; viz., oxalic, acetic, citric, tartaric, etc.

One great advantage possessed by phenolphthalein is that it may be used in alcoholic solutions, or mixtures of alcohol and ether,* and therefore many organic acids insoluble in water may be accurately titrated by its help; in addition to this it may be used to determine the acid combined with many organic bases, such as morphine, quinine, brucine, etc., the base having no effect on the indicator.

Reinitzer† found that phenolphthalein was three times more sensitive in a cold solution than in a hot one.

The following substances can be determined by standard alcoholic potash, with phenolphthalein as indicator. One c.c. normal caustic potash (1 c.c. = ·056 gm. KHO) is equal to—(Hehner and Allen)

·088 gm.	butyric acid.	·1007 gm.	tributyrin.
·282 ,,	oleic acid.	·2947 ,,	triolein.
·256 ,,	palmitic acid.	·2687 ,,	tripalmitin.
·284 ,,	stearic acid.	·2967 ,,	tristearin.
·410 ,,	cerotic acid.	·6760 ,,	myricin.
·329 ,,	resin acids (ordinary colophony, chiefly sylvic acid).		

* H. N. and C. Draper (*C. N.* **55**, 143) have shown that this indicator is rapidly decomposed by atmospheric carbonic acid, which is more readily absorbed by alcohol than by water. Fortunately this is less the case with hot solutions than with cold; titration of this kind should therefore be quickly done, and with not too small a quantity of the indicator.

† See *The Analyst*, 1894, p. 256.

Mixture of Phenolphthalein and Methyl Orange.—This is a neutrality indicator made by dissolving 5 gm. of the first and 1 gm. of the latter in a litre of 50 per cent. alcohol. The neutral point is shown by a lemon-yellow colour. The slightest excess of either acid or alkali shows in turn pink and bright red.

8. **Rosolic Acid, Corallin, or Aurine** ($C_{20}H_{16}O_3$) is soluble in 60 per cent. alcohol, and a convenient strength is 2 gm. per litre. Its colour is pale yellow, unaffected by acids, but turning to violet-red with alkalies. It possesses the advantage over litmus and the other indicators that it can be relied upon for the neutralization of sulphurous acid with ammonia to normal sulphite (Thomson). Its delicacy is sensibly affected by salts of ammonia and by carbonic acid. It is excellent for all the mineral, but useless for the organic acids, excepting oxalic.

9. **Lacmoid.**—This indicator is a product of resorcin, and is therefore somewhat allied to litmus ; nevertheless, it differs from it in many respects, and has a pronounced and valuable character of its own, especially when used in the form of paper. Lacmoid is soluble in dilute alcohol, and the indicator is made by dissolving 3 gm. to the litre.*

10. **Lacmoid Paper.**—This is prepared by dipping slips of calendered unsized paper into the blue or red solution, and drying them.

Thomson states that, in nearly every particular, lacmoid paper, either blue or red, is an excellent substitute for methyl orange, and may be employed in titrating coloured solutions where the latter would be useless. Solution of lacmoid, on the other hand, is not so valuable as the paper, inasmuch as it is more easily affected by weak acids such as carbonic, boric, etc. See p. 42.

There is a large number of other indicators, either in solution or as test papers, and where necessary these will be mentioned.

11. **Congo Red.**—This is specially useful in determining free mineral acids in the presence of most organic acids. A solution of 1 part of the indicator in 100 parts of 10 per cent. alcohol is used. It is red in alkaline solution, turning blue with excess of acid.

12. **Extra Sensitive Indicators.**—Mylius and Förster† describe a series of experiments on the determination of minute traces of alkali and the recognition of the neutrality of water by means of an ethereal solution of iodeosin or erythrosin. This body is a derivative of fluorescin, and occurs plentifully in commerce as a dye for fabrics and paper. The commercial material is purified

* This solution is rendered much more effective as an indicator if Förster's suggestion is adopted, namely, the addition of about 5 gm. of napthol green to a litre of the solution. The effect is to produce a more decided blue colour with alkalies than is given by lacmoid alone.

† *Berichte*, **24**, 1482 ; also *C. N.* **64**, 228, *et seq.*

by solution in aqueous ether, and the filtered solution is shaken with dilute caustic soda, which removes the colour ; the latter is then precipitated with stronger alkali. The salt is then filtered off, washed with spirit and finally recrystallized from hot alcohol. The indicator used by the operators was made by dissolving 1 decigram of the dry powder in a litre of aqueous pure ether. The ether of commerce is purified and rendered neutral by washing with weak alkali, afterwards with pure water, and keeping the ether over pure water. The indicator so prepared is quite useless for the ordinary titration of acids and alkalies ; its chief use is for the detection and measurement of very minute proportions of alkali such as would occur in water kept in glass vessels, or the solubility of calcium or other earthy carbonates in water free from carbonic acid, or in the use of millinormal solutions of alkalies and acids, also the neutrality of so-called pure salts or water. The method of using the indicator is to shake up, say, 20 c.c. with 100 c.c. of the liquid to be examined, when, if alkali is present, a rose colour will be communicated to the layer of ether which rises to the top. The indicator may be used in conjunction with millinormal standard solutions, or colorimetrically, like the well-known Nessler test. Further details of its use are described in the contributions mentioned. Another similar indicator is mentioned by Ruhemann, viz., the imide of dicinnamylphenylazimide.* This material gives a violet rose colour with the most minute traces of alkali, such, for instance, as would appear from merely heating alcohol in a test tube,—the faint trace of alkali thus derived from the glass being sufficient to cause a rapid development of colour.

Another indicator highly sensitive to alkalies has been introduced by Rupp and Loose,† viz., **p**-dimethylamino-azobenzene-**o**-carboxylic acid, which they term "methyl red." It is faintly yellow in alkaline and neutral solutions, and violet-red in acid solutions. A 0·2 per cent solution in alcohol forms the indicator. It can be used to titrate ammonia, even at centinormal strength, as well as some alkaloids, e.g., quinine.

SHORT SUMMARY OF THOMSON'S RESULTS WITH INDICATORS AND PURE SALTS OF THE ALKALIES AND ALKALINE EARTHS.

The whole of the base or acid in the following list of substances may be determined with delicacy and precision unless otherwise mentioned.

Litmus Cold.—Hydrates of soda, potash, ammonia, lime, baryta, etc. ; arsenites of soda and potash, and silicates of the same bases ; nitric, sulphuric, hydrochloric, and oxalic acids.

* *J. C. S. Trans.* **61**, 285.
† *Ber* 1908, **41**, 3905, and *Analyst*, **34**, 29.

Litmus Boiling.—The neutral and acid carbonates of potash, soda, lime, baryta, and magnesia, the sulphides of sodium and potassium, and silicates of the same bases.

Methyl Orange Cold.—The hydrates, carbonates, bicarbonates, sulphides, arsenites, silicates, and borates of soda, potash, ammonia, lime, magnesia, baryta, etc. ; all the mineral acids, sulphites, half the base in the alkaline and alkaline earthy phosphates and arseniates.

Rosolic Acid Cold.—The whole of the base or acid may be determined in the hydrates of potash, soda, ammonia, and arsenites of the same ; the mineral acids and oxalic acid.

Rosolic Acid Boiling.—The alkaline and earthy hydrates and carbonates, bicarbonates, sulphides, arsenites, and silicates.

Phenacetolin Cold.—The hydrates, arsenites, and silicates of the alkalies ; the mineral acids.

Phenacetolin Boiling.—The alkaline and earthy hydrates, carbonates, bicarbonates, sulphides, arsenites, and silicates

Phenolphthalein Cold.—The alkaline hydrates, except ammonia ; the mineral acids, oxalic, citric, tartaric, acetic, and other organic acids.

Phenolphthalein Boiling.—The alkaline and earthy hydrates, carbonates, bicarbonates, and sulphides, always excepting ammonia and its salts.

Lacmoid Cold.—The alkaline and earthy hydrates, arsenites and borates, and the mineral acids. Many salts of the metals which are more or less acid to litmus are neutral to lacmoid, such as the sulphates and chlorides of iron, copper, and zinc ; therefore this indicator serves for determining free acids in such solutions.

Lacmoid Boiling.—The hydrates, carbonates, and bicarbonates of potash, soda, and alkaline earths.

Lacmoid Paper.—The alkaline and earthy hydrates, carbonates, bicarbonates, sulphides, arsenites, silicates, and borates ; the mineral acids ; half of the base in sulphites, phosphates, arseniates.

This indicator reacts alkaline with the chromates of potash and soda, but neutral with the bicarbonates, so that a mixture of the two, or of bichromates with free chromic acid, may be titrated by its aid, which could also be done with methyl orange were it not for the colour of the solutions.

General Characteristics of the Foregoing Indicators.

It is interesting to notice the different degrees of sensitiveness shown by indicators used in testing acids and alkalies. This is well

illustrated by Thomson's experiments, where he used solutions of the indicator containing a known weight of the solid material, and so adjusted as to give, as near as could be judged, the same intensity of colour in the reaction.

It was found that lacmoid, rosolic acid, phenacetolin, and phenolphthalein were capable of showing the change of colour with one-fifth of the quantity of acid or alkali which was required in the case of methyl orange or litmus; that is to say, in 100 c.c. of liquid, where the latter took 0·5 c.c., the same effect with the former was observed with 0·1 c.c.

Another important distinction is shown in their respective behaviour with mineral and organic acids.

It is true the whole of them are alike serviceable for the mineral acids and fixed alkalies; but they differ considerably in the case of the organic acids and ammonia. Methyl orange and lacmoid appear to be most sensitive to alkalies, while phenolphthalein is most sensitive to acids; the others appear to occupy a position between these extremes, each showing, however, special peculiarities. The distinction, however, is so marked, that, as Thomson says, it is possible to have a liquid which may be acid to phenolphthalein and alkaline to lacmoid.

The presence of certain neutral salts has, too, a definite effect on the sensitiveness of certain indicators. Sulphates, nitrates, chlorides, etc., retard the action of methyl orange slightly, while in the case of phenacetolin and phenolphthalein they have no effect. On the other hand, neutral salts of ammonia have such a disturbing influence on the last named indicator as to render it useless, unless special precautions be taken.

Nitrous acid alters the composition of methyl orange; so also do nitrites when existing in any quantity. Forbes Carpenter has noted this effect in testing the exit gases of vitriol chambers.*

Sulphites of the fixed alkalies and alkaline earths are practically neutral to phenolphthalein, but alkaline to litmus, methyl orange, and phenacetolin.

Sulphides, again, can be accurately titrated with methyl orange in the cold, and on boiling off the H_2S a tolerably accurate result can be obtained with litmus and phenacetolin, but with phenolphthalein the neutral point occurs when half the alkali is saturated. The phosphates of the alkalies, arseniates, and arsenites also vary in their effects on the various indicators.

Thomson classifies the usual neutrality indicators into three groups. The *methyl orange group*, comprising that substance, together with lacmoid, dimethylamidobenzene, cochineal and Congo red; the *phenolphthalein group*, consisting of itself and turmeric; and the *litmus group*, including litmus, rosolic acid, and phenacetolin. The methyl orange group are most susceptible to alkalies, the phenolphthalein to acids, and the litmus intermediate between the two. This classification has nothing to do with delicacy of reaction,

* *J. S. C. I.* **5**, 287.

but with the special behaviour of the indicator under the same circumstances; for instance, saliva, which is generally neutral to litmus paper, is always strongly alkaline to lacmoid or Congo red, and acid to turmeric paper. Fresh milk reacts in very much the same way. Such substances are termed *amphoteric*.

Thomson gives the following table as an epitome of the results obtained with indicators, on which several processes have been based. The figures refer to the number of atoms of hydrogen displaced by the monatomic metals, sodium or potassium, in the form of hydrates. Where a blank is left it is meant that the end-reaction is obscure. The figures apply also to ammonia, except where phenolphthalein is concerned and when boiling solutions are used. Calcium and barium hydrates give similar results, except where insoluble compounds are produced. Lacmoid paper acts in every respect like methyl orange, except that it is not affected by nitrous acid or its compounds. Turmeric paper behaves exactly like phenolphthalein with the mineral acids and also with thiosulphuric and organic acids.

Acids.		Methyl Orange.	Phenolphthalein.		Litmus.	
Name.	Formula.	Cold.	Cold.	Boiling.	Cold.	Boiling.
Sulphuric . .	H_2SO_4	2	2	2	2	2
Hydrochloric .	HCl	1	1	1	1	1
Nitric . . .	HNO_3	1	1	1	1	1
Thiosulphuric .	$H_2S_2O_3$	2	2	2	2	2
Carbonic . .	H_2CO_3	0	1 dilute	0	—	0
Sulphurous .	H_2SO_3	1	2	—	—	—
Hydrosulphuric	H_2S	0	1 dilute	0	—	0
Phosphoric .	H_3PO_4	1	2	—	—	—
Arsenic . . .	H_3AsO_4	1	2	—	—	—
Arsenious . .	H_3AsO_3	0	—	—	0	0
Nitrous . . .	HNO_2	indicator destroyed	1	—	1	—
Silicic . . .	H_4SiO_4	0	—	—	0	0
Boric . . .	H_3BO_3	0	—	—	—	—
Chromic . .	H_2CrO_4	1	2	2	—	—
Oxalic . . .	$H_2C_2O_4$	—	2	2	2	2
Acetic . . .	$HC_2H_3O_2$	—	1	—	1 nearly	—
Butyric . .	$HC_4H_7O_2$	—	1	—	1 nearly	—
Succinic . .	$H_2C_4H_4O_4$	—	2	—	2 nearly	—
Lactic . . .	$HC_3H_5O_3$	—	1	—	1	—
Tartaric . .	$H_2C_4H_4O_6$	—	2	—	2	—
Citric . . .	$H_3C_6H_5O_7$	—	3	—	—	—

A. H. Allen clearly points out that the acid which enters into the composition of an indicator must be weaker than the acid which it is required to determine by its means. The acid of which methyl orange is a salt is a tolerably strong one, since it is only completely displaced by the mineral acids; the organic acids are not strong enough to overpower it completely, hence the uncertainty of the end-reaction. The still weaker acids, such as carbonic, hydrocyanic, boric, oleic, etc., do not decompose the indicator at all, hence their salts may be titrated by it just as if the bases only were present.

On the other hand the acid of phenolphthalein is extremely weak, hence its salts are easily decomposed by the organic and carbonic acids. A combination of the two indicators is frequently of service; say, for instance, in a mixture of normal and acid sodium carbonates. If first titrated with phenolphthalein and standard mineral acid, the rose colour disappears exactly at the point when the normal carbonate is saturated; the bicarbonate can then be found by continuing the operation with methyl orange. The study of these new indicators is still somewhat imperfect and requires further elucidation; more especially if we take into consideration some new aspects of the question mentioned in a paper by R. T. Thomson*. The experiments there recorded, which are too voluminous to reproduce here, are of a very interesting character and point to the conclusion that molecular condition, viscosity of the liquid, or some such influence was at work, so as to modify very considerably the action of the indicator. The irregularities occurring in the cases mentioned are no doubt exceptional, and need not disturb the faith hitherto reposed in well-known and much-used methods of titration.

The particular indicator whose erratic action was under discussion was phenolphthalein, and it was demonstrated that in using this indicator in the titration of boric acid with soda no satisfactory end-reaction could be got in a merely aqueous solution, but that by the addition of not less than 30 per cent. of glycerin to the mixture a perfectly correct determination could be made. Other substances such as starch, glucose, and cane sugar had a similar effect, but not to the same extent as glycerin. Mannitol acts just as well.

The result of these investigations is to give a fairly satisfactory method of determining volumetrically boric acid existing in its natural compounds and as a preservative in various kinds of food.

An excellent classification of the more modern indicators as well as those previously described is given by F. Glaser.†

GROUP I. (sensitive to alkalies).

Tropaeolin 00.
Methyl- and Ethylorange, Dimethylamido-azobenzene.
Congo Red, Benzopurpurin, Iodo-esoin, Cochineal.
Lacmoid.

GROUP II.

Fluorescein, Phenacetolin.
Alizarin, Orseille, Hæmatoxylin, Gallein.
Litmus.
p-Nitrophenol, Guaiacum tincture.
Rosolic Acid.

GROUP III. (sensitive to acids).

Tropaeolin 000.
Phenolphthalein, Turmeric, Curcumin W. Flavescin.
a-Naphtholbenzein.
Poirrier's Blue C_4B.

* *J. S. C. I.* **12**, 432.
† *Z. a. C.*, 1899, 273–8; *J. S. C. I.*, 1899, 708.

The above indicators are all either of acid or saline nature, and the classification is based upon the strength of the acid radicle contained in each. Members of Group I. are of strong acid nature, consequently they react readily with bases forming stable salts; they are not sensitive to weak acids. The acid character of the indicators in Group III. is only weakly marked, consequently they are but slightly sensitive to bases; their salts are unstable and easily decomposed by acids. Members of Group II. are intermediate in character between those of Groups I. and III. The table is so drawn up that the sensitiveness of the successive indicators to alkalies decreases as the sensitiveness to acids increases.

The knowledge of the position of an indicator is of importance when bodies are titrated whose basic or acid character is not well marked, *e.g.*, the salts of the mineral acids with alumina, carbonates, silicates, etc. Further, the table enables us to determine to some extent the nature and strength of an acid or base by titrating it with the help of different indicators, *e.g.*, if one acid can be readily titrated with the help of either lacmoid or litmus, and another only with the latter, then the two acids must be of different strengths.

When titrating *formic* acid, lacmoid is a fairly good indicator, but litmus is better; with *acetic* acid a member of Group III. must be used. Here we have a confirmation of the fact that among homologous organic acids with the same number of carboxyl groups the acid character diminishes with increasing molecular weight.

In titrating the alkalies the rule holds good that an indicator only shows the end of a reaction sharply when the product of the change is neutral. The change of colour is only sharp when strong fixed bases are used; ammonium salts being readily hydrolysed by the water present. When very dilute solutions of the fixed bases are used, the colour change is often not sharp; this is due more to the hydrolytic action of the water on the indicator than on the salt formed.

Hydrolytic changes in presence of indicators of Group III. are frequently ascribed to the influence of CO_2 in the air. The author shows experimentally that the fading of the colour of a weak alkaline solution containing phenolphthalein is due more to the hydrolytic action of the water present than to atmospheric CO_2

For Ostwald's Ionization theory of Indicators see his "Scientific Foundations of Analytical Chemistry," translated by McGowan. A. A. Noyes* has published a mathematical treatment of the theory of indicators as applied to volumetric analysis. See also J. T. Hewitt† on the constitution of indicators.

PREPARATION OF THE NORMAL ACID AND ALKALI SOLUTIONS.

It is quite possible to carry out the titration of acids and alkalies with only one standard liquid of each kind; but it frequently happens that standard acids or alkalies are required in other processes of titration besides mere saturation, and it is therefore advisable to have a variety.

Above all things it is absolutely necessary to have at least one standard acid and one standard alkali prepared with the most scrupulous accuracy to use as foundations for all others.

* *J. A. C. S.* 1910, **32**, 815-861, and *J. S. C. I.*, **29**, 1039 (abstr.).

† *Analyst*, 1908, **33**, 85.

It is preferable to use sulphuric acid for the normal acid solution, inasmuch as there is no difficulty commercially in obtaining the purest acid. The normal acid made with it is totally unaffected by boiling, even when of full strength, which cannot be said of either nitric or hydrochloric acid. Hydrochloric acid is, however, generally preferred by alkali makers, owing to its giving soluble compounds with lime and similar bases. Nitric and oxalic acids are also sometimes convenient.

Sodium carbonate, on the other hand, is to be preferred for the standard alkali, because it may readily be prepared in a pure state, or may easily be made from pure sodium bicarbonate as described further on. Differences of opinion exist among chemists as to the best substances to be used as standards in preparing the various solutions used in alkalimetry and acidimetry. My experience satisfies me that, although many of these modifications may serve very well as controls, there is no more reliable standard than pure sodium carbonate.

The chief difficulty with sodium carbonate is that, with litmus as indicator, the titration must be carried on at a boiling heat in order to get rid of CO_2, which obscures the pure blue colour of the indicator, notwithstanding the alkali may be in great excess. This difficulty is now set aside by the use of methyl orange. In case the operator has not this indicator at hand, litmus or phenolphthalein give perfectly accurate results if the saturation is first conducted by rapidly boiling the liquid for a minute after each addition of acid, until the point is reached when one drop of acid in excess gives a change of colour which is not altered by further boiling. This is used as a preliminary test, but as titrations are usually conducted at ordinary temperatures the final adjustment should be made by adding in the second trial a moderate excess of the acid, then boiling to get thoroughly rid of CO_2, rapidly cooling the liquid, and titrating back with an accurate standard alkali. A slight calculation will then give the figures for adjustment. If great accuracy is required this boiling must not take place in glass flasks, but in vessels of porcelain, platinum, or silver, as even Jena glass is affected by boiling alkaline solutions.

As has previously been said, these two standard acid and alkali solutions must be prepared with the utmost care, since upon their correct preparation and preservation depends the verification of other standard solutions.

The best method of preparing sodium carbonate for standardizing sulphuric or hydrochloric acid is to half fill a platinum basin with pure sodium bicarbonate in powder ($NaHCO_3$). Place it in an air bath already heated to about 200° C., and raise the temperature to 270-80°, but not more than 300° C. Let it remain at this temperature for half an hour, then cool it in an exsiccator, and before it is quite cold transfer it to a warm, dry, stoppered tube or bottle, out of which, when cold, it may be weighed rapidly as wanted. The carbonate so produced will be free from lumps and easily soluble in

cold distilled water. To standardize the diluted acid, about 2 or 3 grams of carbonate should be quickly weighed, dissolved in about 80 or 100 c.c. of water, 2 drops of methyl orange solution added, and the operation completed by running the acid of unknown strength, in small quantities at a time, from a burette divided into $\frac{1}{10}$ c.c. into the soda solution until exact saturation is effected.

A second trial should now be made, but preferably with a different weight of the salt. The saturation is carried out precisely as at first. The data for ascertaining the exact strength of the acid solution by calculation are now in hand.

A strictly normal acid should at 15° C. exactly saturate sodium carbonate in the proportion of 100 c.c. to 5·3 gm.

Suppose that 2·46 gm. carbonate required 41·5 c.c. of the acid in the first experiment, then

$$2{\cdot}46 : 5{\cdot}3 :: 41{\cdot}5 : x = 89{\cdot}4 \text{ c.c.}$$

Again: 2·153 gm. carbonate required 36·3 c.c. of acid, then

$$2{\cdot}153 : 5{\cdot}3 :: 36{\cdot}3 : x = 89{\cdot}4 \text{ c.c.}$$

The acid may now be adjusted by measuring 890 c.c. into the graduated litre cylinder, adding 4 c.c. from the burette, or with a small pipette, and filling to the litre mark with distilled water.

Finally, the strength of the acid so prepared must be proved by taking a fresh quantity of sodium carbonate, or by titration with a strictly normal sodium carbonate solution previously made, and using not less than 50 c.c. for the titration, so as to avoid as much as possible the personal errors of measurement in small quantities. If the measuring instruments all agree, and the operations are all conducted with due care, a drop or two in excess of either acid or alkali in 50 c.c. should suffice to reverse the colour of the indicator.

The adoption of sodium carbonate as a standard for preparing normal acid solutions is strongly recommended in Lunge's Report to the International Congress of Applied Chemistry.* From the acid so standardized a corresponding normal caustic alkali may be made, and from that a normal oxalic acid, and from that a decinormal permanganate solution.

Potassium bi-iodate, $KH(IO_3)_2$, an acid salt, which can easily be obtained in a state of great purity, has been recommended for standardizing normal potassium hydroxide, using phenolphthalein as indicator. 3·8995 grams dissolved in water require exactly 10 c.c. of the alkali solution.

Sodium oxalate, prepared as recommended by Sörensen,† is a reliable and accurate standard for acidimetry. It is converted into sodium carbonate by moderate ignition.

C. L. Higgins‡ has discussed the preparation of an exact standard acid in a practical manner.

* *Zeits. f. angew. Chem.*, 1903, **24**, 560, also *Analyst*, **28**, 307.

† *Z. a. C.*, 1903, **42**, 333, and *Analyst* 1903, 306.

‡ *J. S. C. I.*, 1900, **19**, 958.

1. Normal Sodium Carbonate.

53 gm. Na_2CO_3 per litre.

This solution is made by dissolving crystals of pure sodium carbonate, then ascertaining its strength by a correct normal acid at 15°, and adjusting its volume so that it corresponds exactly with the normal acid. Absolutely pure anhydrous sodium carbonate is difficult to find in commerce, and even if otherwise pure is generally contaminated with insoluble dust contracted in the process of drying.

2. Normal Potassium Carbonate.

69·1 gm. K_2CO_3 per litre.

This solution is sometimes, though rarely, preferable to the soda salt, and is of service for the determination of combined acids in certain cases where, by boiling with this reagent, an interchange of acid and base takes place.

It cannot be prepared by direct weighing of the potassium carbonate, and is therefore best made by titrating a solution of unknown strength with strictly normal acid and adjusting as described above.

3. Normal Sulphuric Acid.

49·043 gm. H_2SO_4 per litre.

About 30 c.c. of pure sulphuric acid of sp. gr. 1·840, or thereabouts, are mixed with three or four times the volume of distilled water and allowed to cool, then put into the graduated cylinder and diluted up to about a litre at the proper temperature. The solution may now be titrated with sodium carbonate, as previously described, and accurately adjusted.

Or thus: Suppose that two litres of normal sulphuric acid are required. Counterbalance a beaker with shot on a rough balance and *weigh* into it 104 grams of concentrated sulphuric acid. This is easily done by putting a 5 gm. weight on the pan with the beaker and pouring the acid in a thin stream till it is in excess of the weight, then removing the 5 gm. weight and adding the acid drop by drop till it is the correct weight or a little more. Then pour it into a litre flask containing about 500 c.c. of distilled water, rinse the beaker several times with water, adding the rinsings to the flask, and after shaking the flask allow it to stand several hours till it has acquired the temperature of the laboratory. Now make up to the mark with distilled water, mix, and transfer to the stock bottle. Fill up the litre flask with distilled water and pour this also into the stock bottle. Mix thoroughly and we have a solution rather stronger than normal. Next weigh out 1·06 grams of sodium carbonate and dissolve in about 30 c.c. of water in a Jena beaker. Fill a burette with the acid and run carefully into the soda solution, to which a drop or two of methyl orange has been added, until a pink colour remains after well stirring. Let 18·9 c.c. of the acid be required (instead of 20 for normal). Then the solution requires the addition of 1·1 c.c. of water for every 18·9 c.c. It measures 2000 − 18·9 = (say) 1981 c.c.

$$\therefore\ 18{\cdot}9 : 1981 = 1{\cdot}1 : x.$$
$$x = 115{\cdot}3$$

Now, as an approximation to correct strength with a certainty of being on the right side, pour carefully 110 c.c. of water into the stock bottle, run the liquid from the burette into it, mix thoroughly, fill up the burette twice and then titrate again, using 2·12 grams of the alkali and running the acid into it *slowly*. Suppose that exactly 39·9 c.c. are required (instead of 40). The solution now measures 1981 + 110 − 40 = 2051 c.c. and the amount of water to be added is

$$39{\cdot}9 : 2051 = 0{\cdot}1 : x.$$
$$x = 5{\cdot}1 \text{ c.c.}$$

Add this quantity of water to the bulk, mix thoroughly as before, and the solution should be of exactly normal strength, and should be proved to be so by a final titration with 2·12 grams of sodium carbonate as before.

In the foregoing directions for the preparation of standard acid and alkali it is evident that, with the exception of control by the rather doubtful method of precipitation of the sulphuric acid by barium, the responsibility for an accurate acid solution is thrown upon the sodium carbonate, and though my experience has been that with proper care this is quite reliable, it is plain that any other means of getting at the accurate strength of the sulphuric acid will be acceptable. This is now, owing to the elaborate and careful experiments of Pickering on the specific gravities of solutions of sulphuric acid of various strengths, rendered quite possible.*

It is true that the conditions under which the working strength of the acid is obtained are very stringent, and need the utmost care in performance, but of the extreme accuracy of the result there is no shadow of doubt.

We are indebted to A. Marshall, who has made use of Pickering's figures to calculate a formula and tables, which may be used for making up standard solutions of sulphuric acid with great accuracy and ease. Pickering's percentages are based upon the freezing points of concentrated sulphuric acid, and they are accurate within 0·01 per cent. As practically no volumetric method can be relied upon within less than 0·1 per cent. this leaves an ample margin. Consideration of the figures shows that the strength of the acid can be determined with the necessary accuracy with least difficulty when the acid contains from 60 to 85 per cent. of H_2SO_4. Between these limits an error of 0·001 in the specific gravity or of 1° C. in the temperature will introduce an error of about 0·14 per cent. in the amount of acid, whereas outside the above limits the error introduced may be many times as great.

Method of Procedure: Highly pure sulphuric acid should be taken and diluted with water (preferably by adding the acid to the water). Cool the mixture to a convenient temperature and then determine its specific gravity. The temperature must be known within 0·5° C. and the specific gravity within 0·0005. If a Sprengel tube of 25 c.c. capacity be used, the weighings must be correct within 0·01 gm. The percentage of H_2SO_4 in the acid is then given by the formula

* *J. C. S. Trans.*, 1890. 64–184.

$P = D\ (85{\cdot}87 + {\cdot}05\ T - {\cdot}0004\ t^2) - 69{\cdot}80$
where P = per cent. of H_2SO_4 in the acid
and D = density of the acid at T° C. referred to water at t° C.

The above formula may be used for any temperatures from 0° to 40° C. and for acid containing 62 to 82 per cent. of H_2SO_4. The percentages given by it are correct within $\pm$ ·1 per cent.

The weight of acid required for the preparation of the standard solution can now be calculated.

Let A = grams of H_2SO_4 per litre in the required solution
and n = number of litres required
and W = weight of the acid which must be weighed out
Then

$$W = n\ A \times \frac{100}{P}$$

Weigh out W grams of the acid and make it up to n litres.

The percentages given by the above empirical formula are quite accurate enough for all ordinary purposes; the maximum error which could be introduced by employing them is about 1 in 1,500. More accurate values may, however, be obtained from Tables I. and II.; if great care be exercised, the error in the percentage need not then exceed 1 in 7,000. The weights, on which these tables were based, were fully corrected for air displacement. The weights of acid and water contained by the pyknometer, or Sprengel tube, must therefore be similarly corrected. Unless a very high degree of accuracy be aimed at, this correction may be made by subtracting 0·001 from the uncorrected specific gravity found.

The table at 18° C. (Table II.) is slightly more reliable than that at 15° C. (Table I.), as 18° was one of the temperatures at which Pickering actually determined the densities.*

TABLE I.

For ascertaining the Percentage Strength of Sulphuric Acid Solutions from the Specific Gravities at 15° C. (Water at 15° C. = 1).

Specific Gravity	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
1·60	68·72	68·80	68·89	68·97	69·06	69·15	69·23	69·32	69·40	69·49
1·61	69·58	69·66	69·75	69·84	69·92	70·01	70·09	70·18	70·26	70·35
1·62	70·43	70·52	70·60	70·69	70·77	70·86	70·94	71·03	71·11	71·20
1·63	71·28	71·37	71·45	71·54	71·62	71·71	71·80	71·88	71·97	72·05
1·64	72·13	72·22	72·30	72·39	72·47	72·56	72·64	72·73	72·81	72·90
1·65	72·98	73·07	73·15	73·24	73·32	73·41	73·49	73·57	73·66	73·74
1·66	73·83	73·91	74·00	74·08	74·17	74·25	74·34	74·42	74·51	74·59
1·67	74·68	74·76	74·85	74·93	75·02	75·10	75·19	75·27	75·36	75·44
1·68	75·52	75·61	75·69	75·78	75·86	75·95	76·03	76·12	76·21	76·29
1·69	76·38	76·47	76·55	76·64	76·72	76·81	76·90	76·98	77·07	77·15
1·70	77·24	77·33	77·41	77·50	77·59	77·67	77·76	77·84	77·93	78·02
1·71	78·10	78·19	78·28	78·36	78·45	78·53	78·62	78·71	78·79	78·88
1·72	78·97	79·05	79·14	79·22	79·31	79·40	79·48	79·57	79·65	79·74
1·73	79·83	79·91	80·00	80·09	80·18	80·27	80·37	80·46	80·55	80·64
1·74	80·73	80·82	80·91	81·00	81·10	81·19	81·28	81·37	81·46	81·55
1·75	81·64	81·73	81·83	81·98	82·01	82·11	82·21	82·30	82·40	82·50
1·76	82·60	82·70	82·79	82·89	82·99	83·09	83·19	83·28	83·38	83·48
1·77	83·58	83·68	83·77	83·87	83·97	84·07	84·16	84·26	84·36	84·45

* The figures given in these tables are only applicable to pure sulphuric acid.

TABLE II.

For ascertaining the Percentage Strength of Sulphuric Acid Solutions from the Specific Gravities at 18° C. (Water at 18° C.=1).

Specific Gravity	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
1·60	68·89	68·97	69·06	69·15	69·23	69·32	69·40	69·49	69·58	69·66
1·61	69·75	69·83	69·92	70·01	70·09	70·18	70·26	70·35	70·43	70·52
1·62	70·61	70·69	70·78	70·86	70·95	71·03	71·12	71·20	71·29	71·37
1·63	71·46	71·55	71·63	71·72	71·80	71·89	71·97	72·06	72·14	72·23
1·64	72·31	72·40	72·48	72·57	72·65	72·74	72·82	72·91	72·99	73·08
1·65	73·16	73·25	73·33	73·42	73·50	73·59	73·67	73·76	73·84	73·93
1·66	74·01	74·10	74·18	74·27	74·35	74·44	74·52	74·61	74·69	74·78
1·67	74·86	74·95	75·03	75·12	75·20	75·29	75·37	75·46	75·54	75·63
1·68	75·71	75·80	75·88	75·97	76·05	76·14	76·22	76·31	76·40	76·48
1·69	76·57	75·65	76·74	76·82	76·91	76·99	77·08	77·17	77·25	77·34
1·70	77·42	77·51	77·59	77·68	77·77	77·85	77·94	78·03	78·11	78·20
1·71	78·29	78·37	78·46	78·55	78·63	78·72	78·81	78·90	78·98	79·07
1·72	79·16	79·24	79·33	79·42	79·51	79·59	79·68	79·77	79·85	79·94
1·73	80·03	80·12	80·21	80·30	80·39	80·48	80·57	80·66	80·75	80·84
1·74	80·93	81·02	81·12	81·21	81·30	81·40	81·49	81·58	81·67	81·76
1·75	81·86	81·95	82·04	82·14	82·24	82·34	82·44	82·53	82·63	82·72
1·76	82·82	82·92	83·02	83·13	83·23	83·32	83·42	83·52	83·62	83·72
1·77	83·82	84·92	84·02	84·12	84·22	84·33	84·43	84·54	84·65	84·77

Using these tables I have found that a normal acid of great accuracy may readily be prepared, and the strong solution may be kept intact in strength if placed in a well-stoppered bottle so as to preserve it from damp air. The fact that the concentrated acid is weighed, and not measured, is an additional security, and the weighing may take place within a large range of temperatures without any practical loss of accuracy.

As a check to the normal solution thus made I have used pure sodium carbonate prepared and weighed with the utmost care, and titrated by the help of methyl orange, with the most satisfactory results.*

4. Normal Oxalic Acid.

63·024 gm. $C_2O_4H_2,2H_2O$, or 45·01 gm. $C_2O_4H_2$ per litre.

This solution cannot very well be correctly prepared by direct weighing, owing to uncertain hydration of the crystallized acid; hence it must be titrated by normal alkali of known accuracy, using phenolphthalein as indicator.

The solution is apt to deposit some of the acid at low temperatures, but keeps fairly well if preserved from direct sunlight, and will bear heating without volatilizing the acid. Very dilute solutions of

* For valuable tables giving the relation of specific gravity to percentage for solutions of sulphuric, hydrochloric, and oxalic acids, see a paper by Worden and Motion, *J. S. C. I.* 1905, **24**, 178.

oxalic acid are unstable ; therefore, if a decinormal or centinormal solution is at any time required it should be made when wanted.

5. Normal Hydrochloric Acid.

36·47 gm. HCl per litre.

It has been shown by Roscoe and Dittmar* that a solution of hydrochloric acid containing 20·2 per cent. of the gas when boiled at about 760 mm. pressure loses acid and water in the same proportion, and the residue will therefore have the constant composition of 20·2 per cent., or a specific gravity of 1·10. About 181 gm. of acid of this density, diluted to one litre, serves very well to form an approximately normal acid. Or 120 grams, or 105 c.c., of the ordinary strong hydrochloric acid, which contains about one-third of its weight of the gas, may be diluted with water to one litre, which will then form a solution somewhat stronger than normal. This is now titrated with sodium carbonate exactly as described in section 3, p. 49, and diluted to exact strength.

The actual strength may be determined by precipitation with silver nitrate, or by titration with an exactly weighed quantity of pure sodium carbonate or pure anhydrous calcium carbonate (Iceland Spar). Hydrochloric acid is useful on account of its forming soluble compounds with the alkaline earths, but it has the disadvantage of volatilizing at a boiling heat. Dittmar says that this may be prevented by adding a few grains of sodium sulphate. In many cases this would be inadmissible, for the same reason that sulphuric acid cannot be used. The hydrochloric acid from which standard solutions are made must be free from chlorine gas or metallic chlorides, and should leave no residue when evaporated in a platinum vessel.

G. T. Moody† describes a method of preparing an accurate standard acid which consists in passing gaseous HCl into water and weighing the amount absorbed. This requires a rather delicate arrangement of apparatus, but it is undoubtedly capable of great accuracy when properly carried out.

6. Normal Nitric Acid.

63·02 gm. HNO_3 per litre.

A rigidly exact normal acid should be prepared by means of sodium or calcium carbonate, as in the case of normal hydrochloric acid.

The nitric acid used should be colourless, free from chlorine and nitrous acid, sp. gr. about 1·3. If coloured from the presence of nitrous or hyponitric acid (nitrogen peroxide), it should be mixed with two volumes of water and boiled until colourless. When cold

* *J. C. S.* **12**, 128, 1860. † *J. C. S* Trans. 1898, 658.

it may be diluted and titrated as previously described for sulphuric acid.

Also, 93 grams or 65 c.c. of the ordinary strong nitric acid (sp. gr. 1·42) diluted to one litre gives a solution rather stronger than normal. This is then titrated with sodium carbonate exactly as described in section 3, p. 49, and diluted to exact strength.

7. Normal Alkali Hydroxides.
Caustic Soda, or Potash.

40·01 gm. NaHO or 56·11 gm. KHO per litre.

Pure sodium hydroxide made from metallic sodium may now be readily obtained in commerce, and also powdered caustic soda of 98/99 % purity, and a standard solution may be prepared from either of these. Weigh out rapidly about 42 grams, dissolve in water, make up to a litre, and pour into the stock bottle. When quite cold fill a burette with the solution and titrate with 20 c.c. of normal sulphuric acid to which a drop or two of methyl orange has been added. The solution will be slightly strong and should be carefully adjusted by adding water till of correct strength. The final adjustment should be made by running it into 50 c.c. of normal acid. To make normal potassium hydroxide weigh out 58 grams for a litre.

However pure caustic soda or potash may otherwise be, they are both in danger of absorbing carbonic acid, and hence in using litmus or phenolphthalein the titration must be conducted with boiling. Methyl orange permits the use of these solutions at ordinary temperature notwithstanding the presence of CO_2.

Sodium and potassium hydroxides may now both be obtained in commerce sufficiently pure for all ordinary titration purposes, and their solutions may be freed from traces of chlorine, sulphuric, silicic, and carbonic acids, by shaking with Millon's base, trimercurammonium.* Carbonic acid may also be removed by the cautious addition of barium hydrate in solution, shaking well, and then after settling clear ascertaining the exact strength with correct standard acid.

In preparing these alkali solutions, they should be exposed as little as possible to the air, and when the strength is finally determined, should be preserved in a bottle similar to that shown in fig. 24, or in full bottles having their glass stoppers slightly greased with vaseline.

8. Semi-normal Ammonia.

8·517 gm. NH_3 per litre.

This strength of standard ammonia is useful for saturation analyses in some cases; it is cleanly, does not readily absorb carbonic

* *C. N.* 42, 8.

acid, holds its strength well when kept in a cool place and well stoppered, but is liable to develop flocculent growths. It may, however, be prepared in a few minutes by simply diluting strong liquid ammonia with freshly distilled water. An approximate solution may be made with about 28 c.c. of ·880 ammonia to the litre.

A normal solution cannot be used with safety, owing to evaporation of the gas at ordinary temperatures.*

9. Decinormal Barium Hydroxide.

This solution is best made from the crystallized hydroxide approximately of $^N/_{10}$ strength. This is done by shaking up in a stoppered bottle powdered crystals of barium hydroxide with distilled water, and allowing it to stand a day or two until quite clear. There should be an excess of the hydrate, in which case the clear solution, when poured off into a stock bottle fitted with a tube to prevent the entrance of CO_2 (see fig. 24) will be nearly twice the required strength. It is better to dilute still further (after taking its approximate strength with $^N/_{10}$ HCl and phenolphthalein) with freshly boiled and cooled distilled water; the actual working strength may be checked by evaporating 20 or 25 c.c. to dryness with a slight excess of sulphuric acid, then igniting over a Bunsen flame and weighing the $BaSO_4$. The corresponding acid may be either $^N/_{10}$ oxalic, nitric, or hydrochloric, and the proper indicator is phenolpthalein. Oxalic acid is recommended by Pettenkofer for carbonic acid determination because it has no effect upon the barium carbonate suspended in weak solutions; but there is the serious drawback with oxalic acid that in dilute solution it is liable to lose its strength; therefore, if $^N/_{10}$ oxalic is used it should be freshly prepared from a normal solution.

The bartya solution is subject to constant change by absorption of carbonic acid, but this may be prevented to a great extent by preserving it in the bottle shown in fig. 24. A thin layer of light petroleum oil on the surface of the liquid preserves the baryta at one strength for a long period in the bottle shown in fig. 25.

The reaction between baryta and yellow turmeric paper is very delicate, so that the merest trace of baryta in excess gives a decided brown tinge to the edge of the spot made by a glass rod on the turmeric paper. If the substance to be titrated is not too highly coloured, phenolphthalein should invariably be used.

10. Normal Ammonium-Copper Solution for Acetic Acid and free Acids and Bases in Earthy and Metallic Solutions.

This acidimetric solution is prepared by dissolving pure copper

*Carulla (*J. S. C. I.*, 1907, **26**, 186) gives a series of experiments proving that N/2 ammonia retains its strength with great constancy under varying laboratory conditions.

sulphate in warm water, and adding to the clear solution liquid ammonia until the bluish-green precipitate which first appears is nearly dissolved. The solution is then filtered into the graduated cylinder, and titrated by allowing it to flow from a pipette graduated in $\frac{1}{5}$ or $\frac{1}{10}$ c.c. into 10 or 20 c.c. of normal sulphuric or nitric acid (not oxalic). While the acid remains in excess, the bluish-green precipitate which is produced as each drop falls into the acid rapidly disappears; but so soon as the exact point of saturation is reached, the previously clear solution is rendered turbid by the precipitate remaining insoluble in the neutral liquid.

The process is especially serviceable for the determination of the free acid existing in certain metallic solutions, *i.e.*, mother-liquors, etc., where the neutral compounds of such metals have an acid reaction on litmus—such as the oxides of zinc, copper, and magnesia, and the protoxides of iron, manganese, cobalt, and nickel; it is also applicable to acetic and the mineral acids.

If cupric nitrate be used for preparing the solution instead of sulphate, the presence of barium, or strontium, or metals precipitable by sulphuric acid is of no consequence. The solution is standardized by normal nitric or sulphuric acid; and as it slightly alters by keeping ,a coefficient must be found from time to time by titrating with normal acid, by which to calculate the results systematically. Oxides or carbonates of magnesium, zinc, or other admissible metals, are dissolved in excess of normal nitric acid, and titrated residually with the copper solution.

EXAMPLE: 1 gm. of pure zinc oxide was dissolved in 27 c.c. of normal acid, and 2·3 c.c. of normal copper solution required to produce the precipitate =24·7 c.c. of acid; this multiplied by 0·0405, the coefficient for zinc oxide, =1 gm

DETERMINATION OF THE ACTUAL STRENGTH OF STANDARD SOLUTIONS NOT STRICTLY NORMAL OR SYSTEMATIC.

IN discussing the preparation of the foregoing standard solutions it has been assumed that they shall be strictly and absolutely correct; that is to say, if the same measure be filled first with any alkaline solution, then with an acid solution, and the two mixed together, a perfectly neutral solution shall result, so that a drop or two either way will upset the equilibrium.

Where it is possible to weigh directly a pure dry substance, this approximation may be very closely reached. Sodium carbonate, for instance, admits of being thus accurately weighed. On the other hand, the caustic alkalies cannot be so weighed, nor can the liquid acids. An approximate quantity, therefore, of these substances must be taken, and the exact strength of the solution found by experiment.

In titrating such solutions it is exceedingly difficult to make them so exact in strength that equal volumes, to a drop or two, shall neutralize each other. In technical matters a near approximation may be sufficient, but in scientific investigations it is of the greatest

importance that the utmost accuracy should be obtained; it is therefore advisable to ascertain the actual difference, and to mark it upon the vessels in which the solutions are kept, so that a slight calculation will give the exact result.

Suppose, for instance, that a standard sulphuric acid is prepared which does not rigidly agree with the normal sodium carbonate (not at all an uncommon occurrence, as it is exceedingly difficult to hit the precise point); in order to find out the exact difference it must be carefully titrated as on page 49. Suppose the weight of sodium carbonate to be 1·9 gm., it is then dissolved and titrated with the standard acid, of which 36·1 c.c. are required to reach the neutral point exactly.

If the acid were rigidly exact it should require 35·85 c.c.; in order, therefore, to find the factor necessary to bring the quantity of acid used in the analysis to an equivalent quantity of normal strength, the number of c.c. actually used must be taken as the denominator, and the number which should have been used, had the acid been strictly normal, as the numerator, thus—

$$\frac{35{\cdot}85}{36{\cdot}1} = 0{\cdot}993;$$

0·993 is therefore the factor by which it is necessary to multiply the number of c.c. of that particular acid used in any analysis in order to reduce it to normal strength, and should be marked upon the bottle in which it is kept.

On the other hand, suppose that the acid is too strong, and that 35·2 c.c. were required instead of 35·85,

$$\frac{35{\cdot}85}{35{\cdot}2} = 1{\cdot}0184;$$

1·0184 is therefore the factor by which it is necessary to multiply the number of c.c. of that particular acid in order to bring it to the normal strength. This plan is much better than dodging about with additions of water or acid.

In all circumstances it is safer to prove the strength of any standard solution by experiment, even though its constituent has been accurately weighed in the dry and pure state.

Further, let us suppose that a solution of caustic soda is to be made from carbonate by means of fresh lime. After pouring off the clear liquid, water is added to the sediment to extract more alkali solution; by this means we may obtain two solutions, one of which is stronger than necessary, and the other weaker. Instead of mixing them in various proportions and repeatedly trying the strength, we may find, by two experiments and a calculation, the proportions of each necessary to give a normal solution, thus:—

The exact actual strength of each solution is first found by separately running into 10 c.c. of normal acid as much of each alkali solution as will exactly neutralize it. We have, then, in the case of the stronger solution, a number of c.c. required less than 10. Let us call this number V.

In the weaker solution the number of c.c. is greater than 10, represented by v. A volume of the stronger solution $=x$ will saturate 10 c.c. of normal acid as often as V is contained in x.

A volume of the weaker solution $=y$ will, in like manner, saturate $\frac{10\,y}{v}$ c.c. of normal acid; both together saturate $\frac{10\,x}{V}+\frac{10\,y}{v}$, and the volume of the saturated acid is precisely that of the two liquids, thus—

$$\frac{10\,x}{V}+\frac{10\,y}{v}=x+y.$$

Whence

$$10\,v\,x+10\,V\,y=V\,v\,x+V\,v\,y$$
$$v\,x\,(10-V)=V\,y\,(v-10).$$

And lastly,

$$\frac{x}{y}=\frac{V\,(v+10)}{v\,(10-V)}$$

An example will render this clear. A solution of caustic soda was taken, of which 5·8 c.c. were required to saturate 10 c.c. of normal acid; of another solution, 12·7 c.c. were required. The volumes of each necessary to form a normal solution were found as follows:—

$$5{\cdot}8\,(12{\cdot}7-10\,)=15{\cdot}66$$
$$12{\cdot}7\,(10\quad-5{\cdot}8)=53{\cdot}34$$

Therefore, if the solutions are mixed in the proportion of 15·66 c.c. of the stronger with 53·34 c.c. of the weaker, a correct solution ought to result. The same principle of adjustment is, of course, applicable to standard solutions of every class.

Example: Suppose that 1 litre of normal soda were required. Since $15{\cdot}66+53{\cdot}34=69$ it is clear that the fraction of the stronger solution to be taken is, in all cases,

$\frac{15{\cdot}66}{69}$ or $\frac{1566}{6900}$ or $\frac{522}{2300}$; and to get 1000 c.c. the volume required is

$$\frac{522\times1000}{2300}=\frac{5220}{23}=227 \text{ c.c.},$$

which has to be mixed with $1000-227=773$ c.c. of the weaker solution.

Again: suppose that a standard solution of sulphuric acid has been made approximating as nearly as possible to the normal strength, and its exact value found by titration with sodium carbonate (or a standard hydrochloric acid with silver nitrate), and that such a solution has been calculated to require the coefficient 0·995 to convert it to normal strength. By the help of this solution, though not strictly normal, we may titrate an approximately normal alkali solution thus:—Two trials of the acid and alkaline solution show that 50 c.c. alkali $=48{\cdot}5$ c.c. acid having a coefficient of $0{\cdot}995=48{\cdot}25$ c.c. normal; then, according to the equation, $50\,x=48{\cdot}25$ is the required coefficient for the alkali, *i.e.*

$$x=\frac{48{\cdot}25}{50}=0{\cdot}965.$$

And here, in the case of the alkali solution being sodium carbonate, we can bring it to exact normal strength by a calculation based on the equivalent weight of the salt, thus—

1 : 0·965 : : 53 : 51·145.

The difference between the two latter numbers is 1·855 gm., and this weight of pure sodium carbonate, added to one litre of the solution, will bring it to normal strength.

TABLE FOR THE SYSTEMATIC ANALYSIS OF ALKALIES, ALKALINE EARTHS AND ACIDS.

Substance.	Formula.	Molecular Weight.	Quantity to be weighed so that 1 c.c. Normal Solution = 1 per cent. of substance.	Normal Factor.*
			grams.	
Sodium Oxide . . .	Na_2O	62	3·1	0·031
Sodium Hydroxide .	$NaOH$	40·01	4·00	0·040
Sodium Carbonate . .	Na_2CO_3	106	5·3	0·053
Sodium Bicarbonate .	$NaHCO_3$	84·01	8·40	0·084
Potassium Oxide . .	K_2O	94·2	4·71	0·0471
Potassium Hydroxide .	KOH	56·11	5·61	0·0561
Potassium Carbonate .	K_2CO_3	138·2	6·91	0·0691
Potassium Bicarbonate	$KHCO_3$	100·11	10·01	0·1001
Ammonia	NH_3	17·03	1·703	0·0170
Ammonium Carbonate	$(NH_4)_2\ CO_3$	96·08	4·804	0·0480
Calcium Oxide (Lime) .	CaO	56·09	2·805	0·0280
Calcium Hydroxide .	CaH_2O_2	74·11	3·705	0·0370
Calcium Carbonate .	$CaCO_3$	100·09	5·0	0·050
Barium Hydroxide . .	BaH_2O_2	171·39	8·57	0·0857
Do. (cryst.) . . .	$BaH_2O_2, 8H_2O$	315·51	15·775	0·1578
Barium Carbonate . .	$BaCO_3$	197·37	9·868	0·0987
Strontium Oxide . .	SrO	103·63	5·18	0·0518
Strontium Carbonate .	$SrCO_3$	147·63	7·38	0·0738
Magnesium Oxide . .	MgO	40·32	2·016	0·0202
Magnesium Carbonate .	$MgCO_3$	84·32	4·216	0·0422
Nitric Acid	HNO_3	63·02	6·30	0·063
Hydrochloric Acid . .	HCl	36·47	3·647	0·03647
Sulphuric Acid . . .	H_2SO_4	98·09	4·905	0·04905
Oxalic Acid	$H_2C_2O_4, 2H_2O$	126·06	6·30	0·063
Acetic Acid	$C_2H_4O_2$	60·03	6·00	0·060
Tartaric Acid . . .	$C_4H_6O_6$	150·05	7·50	0·075
Citric Acid	$C_6H_8O_7H_2O$	210·08	7·00	0·070
Carbonic acid . . .	CO_2	44		0·022

* This is the coefficient by which the number of c.c. of normal solution used in any analysis is to be multiplied in order to obtain the amount of pure substance present in the material examined.

If grain weights are used instead of grams, the decimal point must be moved one place to the right to give the necessary weight for examination; thus sodium carbonate, instead of 5·3 gm., would be 53 grains, the normal factor in this case would also be altered to 0·53.

THE TITRATION OF ALKALI SALTS.

1. Total Alkali in Caustic Soda or Potash, or their Carbonates.

THE necessary quantity of substance being weighed or measured, as the case may be, and mixed with distilled water to a proper state of dilution (say about one per cent. of solid material), an appropriate indicator is added, and the solution is ready for the burette. Normal acid is then cautiously added till the change of colour occurs. In the case of caustic alkalies free from CO_2 the end-reaction is very sharp with any of the indicators; but if CO_2 is present, the only available indicators in the cold are methyl orange or lacmoid paper. If the other indicators are used, the CO_2 must be boiled off after each addition of acid.

In examining carbonates of potash or soda, or mixtures of caustic and carbonate, where it is only necessary to ascertain the total alkalinity, the same method applies.

In the examinations of samples of commercial refined soda or potash salts, it is advisable to proceed as follows :—

Powder and mix the sample thoroughly, weigh 10 gm. in a platinum or porcelain crucible, and ignite gently over a spirit or gas lamp, and allow the crucible to cool under the exsiccator. Weigh again, the loss of weight gives the moisture ; wash the contents of the crucible into a beaker, dissolve and filter if necessary, and dilute to the exact measure of 500 c.c. with distilled water ; after mixing thoroughly, take out 50 c.c. (=1 gm.) of alkali with a pipette, transfer to a small flask, bring the flask under a burette containing normal acid and graduated to $\frac{1}{5}$ or $\frac{1}{10}$ c.c., and allow the acid to flow cautiously as before directed until the neutral point is reached. The process may then be repeated, in order to make certain of the correctness of the result.

RESIDUAL TITRATION : As the presence of carbonic acid with litmus and the other indicators, except methyl orange, always tends to confuse the exact end of the process, the difficulty is best overcome, in the case of not using methyl orange, by allowing a known excess of acid to flow into the alkali, boiling to expel the CO_2, cooling, and then cautiously adding normal caustic alkali, drop by drop, until the liquid suddenly changes colour ; by deducting the quantity of caustic alkali from the quantity of acid originally used, the exact volume of acid necessary to saturate the 1 gm. of alkali is ascertained.

This method of re-titration gives a very sharp end-reaction, as there is no CO_2 present to interfere with the delicacy of the indicator. It is a procedure sometimes necessary in other cases, owing to the interference of impurities dissipated by boiling, *e.g.*, H_2S, which would otherwise bleach the indicator—except in the case of methyl orange and lacmoid paper, either of which is indifferent to H_2S in the cold. An example will make the plan clear :

EXAMPLE : 50 c.c. of the solution of alkali prepared as directed, equal to 1 gm. of the sample, is put into a flask, and 20 c.c. of normal acid added ; it is then boiled and shaken till all CO_2 is expelled, and normal caustic alkali added till the neutral point is reached ; the quantity required is 3·4 c.c., which deducted from 20 c.c. of acid leaves 16·6 c.c. The following calculation, therefore, gives the percentage of real alkali, supposing it to be soda :—31 is the half molecular weight of anhydrous soda (Na_2O) and 1 c.c. of the acid is equal to 0·031 gm., therefore 16·6 c.c. is multiplied by 0·031, which gives 0·5146 ; and as 1 gm. was

taken, the decimal point is moved two places to the right, which gives 51·46 per cent. of real alkali. If calculated as carbonate, the 16·6 would be multiplied by 0·053, which gives 0·8798 gm. =87·98 per cent.

The following methods of ascertaining the proportions of mixed alkaline hydroxides, monocarbonates, and bicarbonates must not be taken as absolutely correct, but are correct enough for technical purposes :—

2. Mixed Caustic and Carbonated Alkali Salts.

(*a*) **Precipitation of the carbonate by barium chloride.**—The alkaline salts of commerce consist often of a mixture of caustic and carbonated alkali. If it be desired to ascertain the proportions in these mixtures, the total alkalinity of a weighed or measured quantity of substance (not exceeding 1 or 2 gm.) is ascertained by normal acid and noted ; a like quantity is then dissolved in about 150 c.c. of water in a 200 c.c. flask, and exactly enough solution of barium chloride added to remove all CO_2 from the alkali.

Watson Smith has shown* that whenever an excess of barium chloride is used in this precipitation so as to form barium hydrate, there is invariably a loss of soda : exact precipitation is the only way to secure accuracy.

The flask is now filled up to the 200 c.c. mark with distilled water, securely stoppered, and put aside to settle. When the supernatant liquid is clear, take out 50 c.c. with a pipette, and slowly run in normal hydrochloric acid till neutral. The number of c.c. multiplied by 4 will be the quantity of acid required for the caustic alkali in the original weight of substance, because only one-fourth was taken for analysis. The difference is calculated as carbonate. Or the precipitated barium carbonate may be thrown upon a dry filter, washed well and quickly with boiling water, and titrated with normal acid, instead of the original determination of the total alkalinity ; or both plans may be adopted so that one forms a check to the other.

The principle of this method is that when barium chloride is added to a mixture of caustic and carbonated alkali the CO_2 of the latter is precipitated as an equivalent of barium carbonate, while the equivalent proportion of caustic alkali remains in solution as barium hydroxide. By multiplying the number of c.c. of acid required to saturate this free alkali by the $\frac{1}{1000}$ molecular weight of caustic potash or soda, according to the alkali present, the quantity of substance originally present in this state will be ascertained.

Sörensen and Anderson† have shown that this method only gives trustworthy results if the precipitation with barium chloride be carried out in the warmed solution, and when the latter contains only normal carbonates.

If the solution contains hydroxide or bicarbonate it must be treated with hydrochloric acid or sodium hydroxide before heating and precipitating. The quantity of acid or hydroxide required is ascertained by a previous determination. When a solution of pure normal carbonate is treated, while hot, with an excess of barium chloride, only normal barium carbonate is precipitated ; if, however, the precipitation be performed at the ordinary temperature, more or less acid

* *J. S. C. I.* **1**, 85.

† *Zeit. a.Chem.*, 1908, **47**, 279-294.

carbonate is thrown down, and the supernatant liquid becomes distinctly alkaline. Further, if the solution of the alkali carbonate contains hydroxide, a greater or less quantity of basic barium carbonate is precipitated on treating the hot solution with barium chloride.

As barium hydroxide solution absorbs CO_2 very readily when exposed to the atmosphere, it is preferable to allow the precipitate of barium carbonate to settle in the flask as here described rather than to filter the solution, especially also as the filter obstinately retains some barium hydroxide.

A very slight error, however, occurs in this method in consequence of the volume of the precipitate being included in the liquid in the graduated flask. This error may be obviated by precipitating a small volume of the solution with barium chloride and titrating the liquid and precipitate in the same vessel with normal *oxalic acid* and phenolphthalein, this acid having no action on the barium carbonate.

(*b*) **Use of two indicators.**—On titrating the *cold* solution (as near 0° C. as possible) of mixed hydroxide and carbonate with normal acid and phenolphthalein, keeping tip of burette immersed in the liquid, the colour of the indicator is discharged as soon as all the hydroxide is neutralized and half the carbonate (by conversion into bicarbonate). On adding methyl orange (at most two drops) to the colourless solution and continuing the titration, the solution becomes pink as soon as the remaining half of the carbonate is neutralized. If the first addition of acid $= \mathbf{N}$ c.c., and the second $\mathbf{n}$ c.c., then $\mathbf{N} - \mathbf{n}$ corresponds to hydroxide, 2 $\mathbf{n}$ to carbonate, and $\mathbf{N} + \mathbf{n}$ to total alkali.

3. Determination of Sodium or Potassium Hydroxide in presence of small proportions of Carbonate.

This may be accomplished by means of phenacetolin.*

The alkaline solution is coloured a scarcely perceptible yellow with a few drops of the indicator. The standard acid is then run in until the yellow gives place to a pale rose tint; at this point all the caustic alkali is saturated, and the volume of acid used is noted. Further addition of acid now intensifies this red colour until the carbonate is decomposed, when a clear golden yellow solution results. The neutralization of the NaHO or the KHO is indicated by a rose tint permanent on standing; that of Na_2CO_3 or K_2CO_3 by the sudden passage from red to yellow.

Practice is required with solutions of known composition to accustom the eye to the changes of colour. Phenolphthalein may also be employed for the same purpose as follows:—

Add normal acid to the cold alkaline solution till the red colour is discharged, taking care to use a very dilute solution, and keeping the point of the burette in the liquid so that no CO_2 escapes. The period at which the colour is discharged occurs when all the hydrate is neutralized and the carbonate converted into bicarbonate; the volume of acid is noted, and the solution heated to boiling,

* Lunge, *J. S. C. I.* **1**, 56.

with small additions of acid, till the red colour produced by the decomposition of the bicarbonate is finally destroyed.

In both these methods it is preferable, after the first stage, to add excess of acid, boil off the CO_2, and titrate back with normal alkali. The results are quite as accurate as the method of precipitation with barium.

4. Determination of small quantities of Sodium or Potassium Hydroxide in presence of Carbonates.

A method, by Thomson, consists in precipitating the carbonates by neutral solution of barium chloride in the cold : the barium carbonate being neutral to phenolphthalein, this indicator can be used for the process. When the barium solution is added, a double decomposition takes place, resulting in the formation of an equivalent quantity of sodium or potassium chloride, while the barium carbonate is precipitated and the alkaline hydrate remains in solution.

EXAMPLE (Thomson): 2 gm. of pure sodium carbonate were mixed in solution with ·02 gm. of sodium hydroxide ; excess of barium chloride was then added, together with the indicator, and the solution titrated with $^{N}/_{10}$ acid, of which in three trials an average of 5 c.c. was required ; therefore, $5 \times {·}004 = {·}02$ gm. —exactly the quantity used.

In this process chlorides, sulphates, and sulphites do not interfere ; neither do phosphates, as barium phosphate is neutral to the indicator. With sulphides, half of the base will be determined ; but if hydrogen peroxide be added and the mixture allowed to rest for a time, the sulphides are oxidized to sulphates, which have no effect. If silicates or aluminates of alkali are present, the base will of course be recorded as hydroxide.

Thomson further states :—

" The foregoing method can also be applied to the determination of the hydrates of sodium or potassium in various other compounds, which give precipitates with barium chloride neutral to phenolphthalein, such as the normal sulphites and phosphates of the alkali metals. An illustration of the use to which the facts stated in this and former papers may be put will be found in the analysis of sodium sulphite. Of course sulphate, thiosulphate, and chloride are determined as usual, but to determine sulphite, carbonate and hydrate, or sodium bicarbonate by methods in ordinary use is rather a tedious operation To find the proportion of hydroxide, all that is necessary is to precipitate with barium chloride and titrate with standard acid, as above described. Then, by simple titration of another portion of the sample in the cold, using phenolphthalein as indicator, the hydroxide and half of the carbonate can be found, and finally, by employment of methyl orange as indicator, and further addition of acid, the other half of the carbonate and half of the sulphite can be determined. By simple calculations, the

respective proportions of these three compounds can be obtained, a result which can be accomplished in a few minutes. It must be borne in mind that if a large quantity of sodium carbonate is in the sample the proportion of that compound found will only be an approximation to the truth, as the end-reaction is only delicate with small proportions of sodium carbonate.

5. Determination of Alkali Carbonate and Bicarbonate in the presence of each other.

(*a*) The total alkali is first determined in one portion of the solution by titration with standard acid and methyl orange. To another portion a measured volume of standard sodium hydroxide (free from CO_2) is added, to convert the bicarbonate to carbonate. The sodium carbonate is then precipitated by barium chloride and the excess of hydroxide determined by titration with standard acid as in paragraph 2 (*a*). If **N** c.c. of normal acid correspond to the total alkali, **n** c.c. of normal sodium hydroxide be added, and **n′** c.c. normal acid correspond to the excess of the latter; then, $\mathbf{n} - \mathbf{n}'$ c.c. = bicarbonate, and $\mathbf{N} - (\mathbf{n} - \mathbf{n}')$ c.c. = carbonate. If $\mathbf{n} = \mathbf{N}$, thus ensuring excess of hydroxide, $\mathbf{n}'$ = carbonate. (*b*) **Use of two indicators.**—Titratiug with acid and phenophthalein to neutralization, then with acid and methyl orange, as in paragraph 2 (*b*), the first addition of acid (**n** c.c.) corresponds to half the carbonate, and the second addition (**N** c.c.) to half the carbonate + the total bicarbonate. Thus 2 **n** c.c. = carbonate, and $\mathbf{N} - \mathbf{n}$ = bicarbonate.

This method of titration can be used for soda ash, etc., when carbonate and hydroxide or carbonate and bicarbonate occur in the same solution. [Cf. par. 2 (*b*)]. Should the amount of $^N/_1$ acid used be greater with phenolphthalein than with methyl orange, NaOH is shown to be present, but if greater with methyl orange, then bicarbonate is present, and calculations for carbonate and hydrate, or carbonate and bicarbonate, are made in the usual way.

6. Determination of Alkalies in the presence of Sulphites.

It is not possible to determine the alkaline compounds in the presence of sulphites by titration with acids, as a certain quantity of acid is taken up by the sulphite, SO_2 being evolved. This difficulty may be completely overcome by the aid of hydrogen peroxide, which speedily converts the sulphites into sulphates.* These operators proved that neither caustic nor carbonated alkali was affected by H_2O_2, nor had the latter any prejudicial effect on methyl orange in the cold. The quantity of H_2O_2 required in any given analysis must depend on the amount of sulphite present;

* Grant and Cohen, *J. S. C. I.* **9**, 19.

for instance, the caustic salts of commerce contain about 50 % of sulphite, and it suffices to take 10 c.c. of ordinary 10 vol. H_2O_2 for every 0·1 gm. of the salts in solution. In the case of mixtures containing less or more sulphite the quantity may be varied.

METHOD OF PROCEDURE: A measured volume of the peroxide is run into a beaker, and three or four drops of methyl orange added. As the H_2O_2 is invariably faintly acid, the acidity is carefully corrected by adding drop by drop from a pipette $^N/_{100}$ caustic soda. The required quantity of salt to be analyzed is then added in solution, and the mixture gently boiled, whereby the methyl orange will be bleached. The liquid is then cooled, a drop or two more of methyl orange added, and the titration for the proportion of alkali carried out with normal acid. The results are very satisfactory.

7. Determination of Caustic Soda or Potash by standard Potassium Dichromate.

This process, or rather the inverse of it, was devised by Richter, for determining dichromate with caustic alkali by the aid of phenolphthalein. Exact results may be obtained by it in titrating soda or potash as hydrates, but not ammonia as recommended by Richter.

For the process there are required a decinormal solution of bicarbonate containing 14·72 gm. per litre, and $^N/_{10}$ soda or potash solution titrated against sulphuric acid. A comparison liquid containing about 1 gm. of potassium chromate in 150 – 200 c.c. water is advisable for ascertaining the exact end of the reaction; 50 c.c. of the alkali, having been diluted with the same volume of water, is coloured with phenolphthalein, and the dichromate run in from a burette; the fine red tint changes to reddish yellow, which remains till the neutral point is nearly reached, when the yellow colour of the chromate is produced. The change is not instantaneous, as with mineral acids, so that a little time must be allowed for the true colour to declare itself.

8. Direct Determination of Sodium by Potassium dihydroxytartrate and Permanganate.

An interesting series of researches on the oxidation products of tartaric acid has been published by H. J. Horstman Fenton, M.A.* The results of these researches have been to develop the only method of obtaining sodium in such a form of combination as to admit of its volumetric determination. The author has kindly furnished me with specimens of dihydroxytartaric acid, and also of the potassium salt, with which to verify the results obtained by him, and I am able to state that when the method is carried out with extreme care and strict attention to details it is capable of giving satisfactory results.

Dihydroxytartaric acid, so far as present knowledge is concerned, is best prepared from dihydroxymaleic acid, and as both these acids are comparatively unknown their preparation will now be described.

Preparation of Dihydroxymaleic Acid.—Tartaric acid is dissolved in the least possible quantity of hot water; finely-divided iron (*ferrum redactum*) is added,

* *J. C. S. Trans.*, 1894, pp. 899–910, 1898, pp. 71–81, *ibid*, 472–482, and on the volumetric determination of sodium 1898, pp. 167–174.

and the liquid boiled until all the iron has disappeared. The quantity of iron must be insufficient to cause a separation of ferrous tartrate when the action is finished; about $\frac{1}{250}$ part of the weight of tartaric acid employed answers well, but the final result does not appear to be much influenced by the proportion of iron in solution, at any rate within considerable limits. The solution, filtered, if necessary, through cotton wool, is carefully cooled, surrounded by ice, and hydrogen peroxide (20 volume) added in small quantities at a time, allowing a few minutes to elapse between each addition. The first portions of the peroxide merely produce a yellowish colour, but, as the action proceeds, each addition produces a dark green or nearly black appearance, transient at first, but becoming more and more persistent. When this dark colour remains for two or three minutes, it is a rough indication that sufficient peroxide has been added. Great care must be taken not to add an excess of the peroxide, or the whole of the material will be wasted. Nordhausen sulphuric acid is now added by means of a thistle funnel, drawn out to a fine point, in very small quantities at a time, cooling carefully between each addition, preferably by ice and salt. The quantity added is a matter of importance, too much or too little giving an indifferent yield of the substance; the best proportion is found by experience to be about $\frac{1}{10}$th of the total volume of the liquid operated on. The mixture, still surrounded by ice, is put aside in a cold place, and after a few hours crystals begin to form. The first deposit is often discoloured and the crystals small, but the subsequent crops are beautifully white and pure. If the experiment is properly conducted, and the liquid kept sufficiently cool, crystals continue to form for several days, but the greater part are deposited within about 24 hours.

The crystals are collected with the aid of a pump, carefully drained, and washed repeatedly with small quantities of cold water. After again thoroughly draining, they are spread on filter-paper and air-dried. They appear to undergo no change in the air, even after several weeks' exposure.

Preparation of Dihydroxytartaric Acid.—Crystallized dihydroxymaleic acid as above described ($C_4H_4O_6,2H_2O$) is well triturated with from 4 to 5 times its weight of glacial acetic acid, and rather more than the calculated quantity of bromine (1 mol. acid to 1 mol. bromine) dissolved in a little glacial acetic acid, is added to the mixture in small portions at a time. The first portions are almost instantly bleached, bnt the action afterwards becomes more sluggish and apparently ceases. A few drops of water are then added, whereupon the colour of the bromine is again immediately discharged. The addition of bromine is continued until the colour is quite permanent on standing, even when a drop or two of water is added. This final stage is reached when the bromine has been added in about the calculated proportion; fumes of hydrogen bromide are freely evolved during the operation. The dihydroxymaleic acid is nearly insoluble in cold glacial acetic acid, but when the oxidation is finished complete solution takes place. The solution is allowed to stand for an hour or two and then vigorously stirred, when the dihydroxytartaric acid quickly, sometimes suddenly, separates as a heavy, white, crystalline powder.

The product is now collected and drained with the aid of the pump, washed once or twice with small quantities of anhydrous ether, and kept in a vacuum desiccator over solid potash and sulphuric acid to remove the last traces of hydrobromic and acetic acids, bromine and ether. The yield of purified product thus obtained is 70 per cent. or more of the theoretical. The formula for this acid is $C_4H_6O_8$.

The acid just described was first studied in relation to potassium permanganate by Fenton, and the reaction found to be quite definite; and bearing in mind the very sparingly soluble character of sodium dihydroxytartrate it appeared probable that a simple volumetric method for sodium might be devised. For complete precipitation it is necessary that the free acid shall be exactly neutralized, and this is most conveniently effected by first preparing the normal potassium salt. The employment of this salt as precipitant has also the advantage that risk is avoided of the pre-

cipitation of potassium with the sodium salt when the former metal is present in the mixture analyzed.

Preparation of Potassium Dihydroxytartrate.—Weigh equivalent proportions of the acid 182, and dry potassium carbonate 138 parts. Dissolve separately in the least possible quantity of ice cold water, then mix in a vessel surrounded by ice, and stir. Crystals soon separate, which may then be collected on a filter, and finally dried on changes of filter-paper in the air or in a desiccator. The salt so obtained does not, however, keep in proper condition for more than a few days, and therefore it is better to prepare it specially when sodium determinations have to be made. The formula of the salt is $K_2(C_4H_4O_8)H_2O$.

Standardizing the Permanganate Solution.—In this method of titrating soda it is preferable to standardize the permanganate upon pure sodium chloride rather than to depend on the relations between the acid and permanganate. The strength of the latter solution is best about $^N/_5$, *i.e.*, 6·321 gm. of $MnKO_4$ to the litre. Its strength as regards the sodium to be determined is ascertained by the following procedure, bearing in mind that exactly the same process in every respect must be carried out in determining sodium in any given salt.

Method of Procedure: About 0·2 gm. of pure sodium chloride is accurately weighed and dissolved in a small beaker with the least possible quantity of water, then placed in a basin and surrounded by ice. Then an excess, say 0·8 gm. of the potassium salt is weighed and dissolved in another small beaker, with not more than 25 c.c. of ice cold water, placed in ice and stirred till dissolved; this occurs with some difficulty, but if the liquid is not free from floating particles or deposit, it must be quickly filtered into the sodium solution still standing in ice. The mixture is then allowed to stand in ice for half an hour with occasional stirring. The precipitated sodium salt is then collected by means of a small filter on filter plate and quickly drained with the water pump, then washed with 3 or 4 c.c. of ice cold water three or four times in succession, and rinsing out the precipitating beaker. Finally, the precipitate is dissolved through the filter in a large excess of dilute H_2SO_4, rinsing out the precipitating beaker with dilute acid in the process, and titrated with the permanganate at ordinary temperature. The action on the permanganate is at first very slow, but when once commenced increases in force like the action of oxalic acid, and the end is quite distinct. The volume of permanganate having been noted, its working strength in relation to sodium in any available compound is ascertained, and marked on the bottle.

Example: 0·21 gm. of pure NaCl was treated strictly according to the procedure just described, and required 48·3 c.c. of permanganate, not strictly $^N/_5$, but about that strength. The same weight of the same NaCl was then taken with about the same quantity of pure KCl in the same manner. The volume of permanganate used was 48·9 c.c. Taking into account the large volume of permanganate required for so small a quantity of sodium the difference was infinitesimal as regards the amount of sodium found. Practice undoubtedly renders the results more certain if exactly the same conditions are observed, more especially in keeping the temperature down to as near 0° as possible.

The process seems complicated, but when once the cooling arrangements are satisfactorily made it becomes very simple, and if there are a series of sodium determinations to be made such as the alkali chlorides in mineral water residues, etc., it is far more rapid, and probably more exact than the determination of the potassium by platinum, and calculating the sodium by difference.

It must be noted that the method is not available, so far as is known, in the presence of metals other than sodium, potassium, and magnesium. Ammonium should be removed, and borax cannot accurately be examined for its sodium. The metals should preferably be present as chlorides, sulphates, or nitrates; carbonates and hydroxides of sodium must be neutralized exactly with one of the mineral acids.

9. Determination of Potassium by means of Sodium Cobaltinitrite.

Sodium cobaltinitrite [$Na_3Co\ (NO_2)_6$] under the name of de Koningh's reagent has long been known as a valuable qualitative test for potassium, with solutions of which it gives a canary-yellow precipitate. Its use for the quantitative determination of potassium, both gravimetrically and volumetrically, has been investigated by Adie* who, on adding a solution of sodium cobaltinitrite to a potassium salt, obtained a compound to which he gave the formula $K_2NaCo\ (NO_2)_6,H_2O$. The amount of K_2O in the precipitate may be found by means of a decinormal solution of permanganate. Cunningham and Perkin† have recently shown, however, that the precipitate may be a mixture of the tri- and di-potassium salts, $K_3Co\ (NO_2)_6$ and $K_2NaCo\ (NO_2)_6$, and emphasize the difficulty, also referred to by Adie, of washing the precipitate so as to obtain a clear filtrate. The constitution of the precipitate is shown to depend on whether the sodium cobaltinitrite or the potassium salt is in excess. Hence the authors consider that this method cannot be recommended for the analysis of potassium or cobalt compounds.

10. Titration of Organic Salts of the Alkalies.

The following organic salts yield alkali carbonate on ignition. When the latter, in aqueous solution, is titrated with normal acid, the number of c.c. used multiplied by the factor tabulated below gives the weight of the corresponding salt.

Name of Salt.	Formula.	Normal Factor.	Logarithm.
Sodium acetate . .	$NaC_2H_3O_2.\ 3H_2O$	0·13608	$\bar{1}$·13379
,, benzoate . . .	$Na\ C_7H_5O_2$	0·14404	$\bar{1}$·15848
,, salicylate . .	$Na\ C_7H_5O_3$	0·16004	$\bar{1}$·20423
Potassium acetate . .	$K\ C_2\ H_3\ O_2$	0·09812	$\bar{2}$·99176
,, bitartrate . .	$KHC_4H_4O_6$	0·18814	$\bar{1}$·27448
,, citrate . .	$K_3C_6H_5O_7.\ H_2O$	0·10812	$\bar{1}$·03391
,, tartrate . .	$2K_2C_4H_4O_6.\ H_2O$	0·11762	$\bar{1}$·07048
,, & sodium tartrate	$KNaC_4H_4O_6.\ 4H_2O$	0·14110	$\bar{1}$·14953

TECHNICAL EXAMINATION OF SOME ALKALI COMPOUNDS FOUND IN COMMERCE OR PRODUCED IN COURSE OF MANUFACTURE.

There is now considerable unanimity among English and foreign manufacturers of alkali compounds as to methods of analysis to be adopted either for guidance in manufacture or for commercial

* *J. C. S.* 1900, **77**, 1076; see also W. A. Drushel; *Zeit. Anal. Chem.* 1907, **56**, 223 1908, **59**, 97; *Analyst*, **33**, 35 and 378.

† *J. C. S.*, 1909, **95**, 1562.

valuation. Lunge* has contributed important papers on the subject, also in conjunction with Hurter in the *Alkali Makers' Handbook*,† which contains valuable tables and processes of analysis. So far as volumetric methods are concerned, the same processes will be given here, together with others.

11. Soda Ash, Black Ash, Mother-liquors, etc.

Soda Ash or Refined Alkali.—5 or 10 gm. are dissolved in about 150 c.c. of warm distilled water, and any insoluble matter filtered off (German chemists do not filter), and the volume diluted to ½ or 1 litre.

The *total alkali* is determined in 50 c.c. by normal sulphuric, nitric, or hydrochloric acid, as on page 60. 1‡

The *caustic alkali* present in any sample is determined as on page 61. 2.

The presence of sulphide is ascertained by the smell of sulphuretted hydrogen when the alkali is saturated with an acid, or by dipping paper steeped in sodium nitro-prusside into the solution: if the paper turns blue or violet, sulphide is present.

The quantity of *sulphide and sulphite* may be determined by saturating a dilute solution of the alkali with a slight excess of acetic acid, adding starch, and titrating with $^N/_{10}$ iodine solution till the blue colour appears. The quantity of iodine required is the measure of the sulphuretted hydrogen and sulphurous acid present.

The proportion of *sulphide* is determined as follows: 13·820 gm. of pure silver are dissolved in dilute nitric acid, and the solution together with an excess of liquid ammonia made up to a litre. Each c.c. =0·005 gm. Na_2S.

METHOD OF PROCEDURE: 100 c.c. of the alkali liquor is heated to boiling, some ammonia added, and the silver solution dropped in from a burette until no further precipitate of Ag_2S is produced. Towards the end, filtration will be necessary in order to ascertain the exact point, to which end the Beales filter is serviceable (fig. 23). The amount of Na_2S so found is deducted from the total sulphide and sulphite found by iodine.

Sodium chloride (common salt) may be determined by carefully neutralizing 1 gm. of the alkali with nitric acid, and titrating with decinormal silver solution and potassium chromate. Each c.c. represents 0·005846 gm. of common salt. Since the quantity of acid necessary to neutralize the alkali has already been found, the proper measure of $^N/_{10}$ nitric acid may at once be added.

Sodium sulphate is determined either directly or indirectly, as under Sulphuric Acid. Each c.c. of normal barium chloride is equal to 0·071 gm. of dry sodium sulphate.

Examination of Crude Soda Lyes and Red Liquors.—Kalmann and Spüller§ recommend a process based on the insolubility of barium sulphite and the solubility of barium thiosulphate in alkaline solutions. The determination is performed in the following manner:—1.—The total alkalinity is determined in a measured volume of the liquor under examination by titration with normal acid, methyl orange being used as indicator. The acid consumed equals sodium carbonate + sodium sulphide + sodium hydroxide, + one-half the sodium sulphite present (Na_2SO_3 is alkaline and $NaHSO_3$ neutral to methyl orange). 2.—An equal volume of the liquor is titrated with $N/_{10}$ solution of iodine, the volume consumed corresponding with the sodium sulphide + the sodium sulphite + the sodium thiosulphate. 3.—Twice the volume of liquor used in (1) and (2) is precipitated with an alkaline zinc solution, and the mixture made up to a certain

* *J. S. C. I.* **1**, 12, 16, 55, 92.

† This work now appears in an extended form under the title of *Technical Chemists' Handbook.* (Gurney & Jackson, 1908.)

‡ This gives a slight error, owing to traces of aluminate of soda and lime, which consume acid.

§ *Dingl. polyt. J.*, 264, 456–459.

measure, one-half of which is filtered, acidified, and titrated with $^N/_{10}$ iodine. The iodine consumed equals sodium sulphite + thiosulphate. 4.—Three or four times the volume of liquor used in (1) and (2) is treated with an excess of a solution of barium chloride, the mixture made up to a known volume with water, and filtered. (*a*) One-third or one-fourth (as the case may be) of the filtrate is titrated with normal acid the amount used corresponding with the sodium hydroxide + the sodium sulphite. (*b*) A further third or fourth of the filtrate is acidified and titrated with $^N/_{10}$ iodine, the iodine consumed being equal to sodium sulphite + sodium thiosulphate. The calculation is made as follows:—

2 —4*b*	...... = A c.c. $^N/_{10}$ iodine corresponding to	....	Na_2SO_3
2 —3	...... = B c.c. $^N/_{10}$ iodine corresponding to	....	Na_2S
4*b*—(2—3)	.. = C c.c. $^N/_{10}$ iodine corresponding to	....	$Na_2S_2O_3$
4*a*—$\frac{1}{10}$B	.... = D c.c. normal acid corresponding to	....	NaOH
1 —(4*a* + $\frac{1}{10}$A)	= E c.c. normal acid corresponding to	....	Na_2CO_3

Black Ash.—Digest 50 gm. with warm water in a half-litre flask, fill up to mark, shake, and allow to stand till settled.

(1) *Total Alkali* existing as carbonate, hydrate, and sulphide, is found by titrating 10 c.c. of the clear liquid (= 1 gm. of ash) with standard acid and methyl orange in the cold.

(2) *Caustic Soda.*—20 c.c. of the liquid are put into a 100 c.c. flask with 10 c.c. of solution of barium chloride of 10 per cent, strength, filled up with hot water, well shaken, and corked after settling a few minutes. The clarified liquid is filtered, and 50 c.c. (= 1 gm. ash). titrated with standard acid and methyl orange; or it may be titrated without filtration if standard oxalic acid and phenolphthalein are used, this acid having no effect on the barium carbonate. Each c.c. normal acid = 0·031 Na_2O. This includes sulphides.

(3) *Sodium Sulphide.*—Put 10 c.c. of liquor into a flask, acidulate with acetic acid, dilute to about 200 c.c. and titrate with $^N/_{10}$ iodine and starch. Each c.c. = 0·0039 Na_2S, or 0·0031 Na_2O.

(4) *Sodium Chloride.*—10 c.c. are neutralized exactly with normal nitric acid, and boiled till all H_2S is removed. Any sulphur which may have been precipitated is filtered off, and the filtrate titrated with $^N/_{10}$ silver and chromate. Each c.c. = 0·005846 gm. NaCl.

(5) *Sodium Sulphate.*—This is best determined by precipitation as barium sulphate, and weighing, the quantity being small. If, however, volumetric determination is desired, it may be done as under Sulphuric Acid, taking 50 c.c. of liquor.

For other methods of examining the various solid and liquid alkali wastes used for soda and sulphur recovery, etc., the reader is referred to the *Technical Chemists' Handbook* already mentioned.

12. Salt Cake.

This is the somewhat impure sodium sulphate used in alkali manufacture or left in the retorts in preparing hydrochloric acid from sulphuric acid and salt.

Free acid is determined by dissolving 20 gm. of the sample, diluting to 250 c.c., taking out 50 c.c. (= 4 gm. salt cake) with a pipette, adding methyl orange, and titrating with standard sodium carbonate. The total acidity is calculated as SO_3, including HCl and $NaHSO_4$.

The *common salt* present is determined by decinormal silver solution and potassium chromate, having first saturated the free acid with pure sodium carbonate; 1 c.c. silver solution is equal to 0·005846 gm. of salt.

Sulphuric acid, combined with soda, is determined either directly or indirectly as under Sulphuric Acid; 1 c.c. of normal barium solution is equal to 0·071 gm. of dry sodium sulphate.

Iron is precipitated from a filtered solution of the salt cake with ammonia in excess, the precipitate of ferric hydrate re-dissolved in sulphuric acid, reduced to the ferrous state with zinc and titrated with permanganate.

13. Soap.

The following is a *resumé* of the methods given for the analysis of soaps by Lewkowitsch.*

(1) *Water.*—This is usually found by difference. The sum of the percentages of fatty anhydrides and alkali in its various forms subtracted from 100 gives the water. For direct determination in exceptional cases about 5 grams,—carefully taken from the centre of a cake by cutting away all the outer portions—in thin shavings are put into a porcelain dish and weighed with a glass rod, which is used from time to time to break the skin that forms on drying and prevents the escape of water from the inner portions. Dry at 100° C. till of constant weight.

(2) *Fatty matter and total alkali.*—Weigh accurately 5—10 gm. of the sample and dissolve, with constant stirring, in hot water in a beaker or porcelain dish, heating gently. Add a few drops of methyl orange and acidify with a known volume of normal HCl or H_2SO_4. Heat with constant stirring until the separated fatty acids have melted into oily drops. Add a known weight (about 5 gm.) of dry beeswax or paraffin wax, and heat again until the mixture of fatty matter and wax appears as a clear, transparent layer on the surface of the liquid. Remove the stirrer, after rinsing with boiling water, heat till the fatty matter again collects into one mass, remove the vessel from the source of heat and set aside in a cool place. The solid cake that forms on the surface is then removed by means of a platinum spatula, rinsed with cold water and placed on filter paper. The sides of the vessel are carefully scraped and the scrapings added to the cake. The cake is dried by touching lightly with filter paper and placed bottom upwards on a watch glass, allowed to dry in a desiccator and weighed. The weight thus obtained, less the wax added, gives the *fatty matter*. If neutral fat, wax and unsaponifiable matter are absent, the result may be returned as *fatty acids* (rosin acids are regarded as so much fatty acids). In a complete analysis of a soap the fatty acids are multiplied by 0·9675 and the value so obtained returned as *fatty anhydrides*. The latter form a direct measure of the actual amount of soap present.

The acid liquid is filtered to remove traces of fatty acids and titrated back with $^N/_2$ soda or potash. The *total alkali* thus obtained is calculated to Na_2O in the case of hard soaps and to K_2O in the case of soft soaps.

(3) Free *caustic alkali.*—Dissolve a weighed portion of the soap in absolute alcohol and filter. The alkaline salts remain on the filter and the titration of the alcoholic filtrate with $^N/_{10}$ HCl, using phenolphthalein as indicator, gives the result required.

Should the alcoholic solution be acid, it must be titrated with $^N/_{10}$ alkali and the latter calculated to *free fatty acids*, expressed as oleic.

(4) The precipitate on the filter in (3) may contain carbonate, silicate, borate, etc. It is washed with cold water and the filtrate titrated with $^N/_{10}$ acid, using methyl orange as indicator. The number of c.c. used calculated as Na_2O give the alkali contained in the alkaline salts.

The sum of (3) and (4) subtracted from (2), gives the *combined alkali*.

In valuing a hard soap it should be noted that the presence of more than 64 per cent. of fatty acids shows that the soap has either dried spontaneously on keeping or been dried artificially; a less percentage indicates the presence of an excess of water or of alkali, or some adulterant.

A genuine potash soap (soft soap) should theoretically have the following composition:—

Fatty anhydrides	38·70 %
Combined potassium oxide (K_2O)	6·84
Glycerol, water, and potassium carbonate	54·46
	100·00

* *Oils, Fats and Waxes*, 4th edition, vol. iii., p. 287 et seq.

TITRATION OF ALKALINE EARTHS AND THEIR COMPOUNDS.

STANDARD hydrochloric or nitric acid must in all cases be used for the titration of the caustic or carbonated alkaline earths, as these are the only acids yielding soluble compounds, except in the case of magnesia. In titrating the oxides, such as caustic lime, baryta, strontia, or magnesia, any of the indicators may be used and the residual method should be adopted, viz., adding a known excess of standard acid, boiling to expel any trace of carbon dioxide, and then titrating the residual free acid by means of standard alkali.

The carbonates of the same bases may, of course, also be determined in the same way, bearing in mind that when methyl orange is used the liquid is best cooled before the final titration. All heating may be avoided when using methyl orange in titrating mixtures of oxides or hydroxides and carbonates, or the latter only, unless it is impossible to dissolve the substance in the cold. A good excess of acid is generally advisable.

The total amount of base in mixtures of caustic and carbonated alkaline earths is also determined in the same way.

(1) **Determination of Mixed Hydroxides and Carbonates.**—This may be done using either phenacetolin or phenolphthalein as indicator. The former has been recommended by Degener and Lunge: the method, however, requires practice in order to mark the exact change of colour.

METHOD OF PROCEDURE: The liquid containing the compound in a fine state of division is tinted with phenacetolin so as to be of a faint yellow; normal acid is then cautiously added until a permanent pink occurs (at this stage all the hydroxide is saturated), more acid is now cautiously added until the colour becomes deep yellow,—the volume of acid so used represents the carbonate.

The method is especially adapted to mixtures of calcium hydroxide and carbonate. It is also applicable to barium, but not to magnesium, owing to the great insolubility of magnesium hydroxide in dilute acid.

If phenolphthalein is used as indicator, the method is as follows:

Heat the liquid to boiling, and cautiously add normal acid until the red colour is just discharged. The carbonates of calcium and barium, rendered dense by boiling, are both quite neutral to the indicator. To obtain the whole of the base, excess of normal acid is used, and the mixture re-titrated with normal alkali.

Magnesium in solution as bicarbonate may be accurately determined in the cold with methyl orange as indicator.

(2) **Determination of Calcium, Barium, Magnesium and Strontium in Neutral Soluble Salts.**—The amount of base in the chlorides and nitrates of the alkaline earths may be readily determined as follows:—

The weighed salt is dissolved in water, cautiously neutralized if acid or alkaline, phenolphthalein added, heated to boiling, and normal sodium carbonate delivered in from time to time with boiling until the red colour is permanent.

Magnesium salts cannot, however, be determined in this way, or even mixtures of lime and magnesia, as magnesium carbonate affects the indicator in a different manner from the other carbonates.

Nitrate of Lime (atmospheric). The nitrogen in this fertiliser may be indirectly determined by titrating the calcium present as nitrate with standard sodium carbonate.

The nitrate of lime must not contain the following:—(*a*) Nitrates of metals, the carbonates of which are soluble in water (alkali nitrates); (*b*) soluble oxides of metals, the carbonates of which are soluble in water (alkali oxides); (*c*) soluble salts of metals, the carbonates of which are insoluble in water, except nitrites and nitrates (*e.g.*, $MgSO_4$, $CaCl_2$). I have found that these conditions are fulfilled by the leading brand of this fertiliser now on the English market, and this indirect method gives quite satisfactory results in comparison with the reduction and distillation process.

METHOD OF PROCEDURE: 10 grams Nitrate of Lime [containing about 80 °/$_\circ$ $Ca(NO_3)_2$] are dissolved in water and made up to 500 c.c. without filtration. 50 c.c. are transferred to a beaker or conical flask and 50 c.c. $^N/_5$ sodium carbonate added, boiled, and the precipitated calcium carbonate together with other insoluble substances, if present, filtered off. In the cooled filtrate the excess of sodium carbonate is titrated with $^N/_5$ hydrochloric acid and methyl orange. The Na_2CO_3 consumed corresponds to the $Ca(NO_3)_2$ present.

$$1 \text{ c.c. } ^N/_5 \ Na_2CO_3 = \cdot 0028 \text{ gram N.}$$

Should the nitrate of lime contain free lime, this does not affect the titration, as an amount of sodium hydroxide is formed in the filtrate equivalent to the sodium carbonate consumed by the calcium hydroxide.

EXAMPLE: 50 c.c. of solution (=1 gm. salt) + 50 c.c. $^N/_5$ Na_2CO_3 required 2·3 c.c. $^N/_5$ HCl. $50 - 2{\cdot}3 = 47{\cdot}7$ c.c. $^N/_5$ Na_2CO_3 consumed. $47{\cdot}7 \times {\cdot}0028 \times 100 = 13{\cdot}35$ °/$_\circ$ Nitrogen.

(3) **Precipitation of the Alkaline Earths from their Neutral Salts as Carbonates.**—Soluble salts of calcium, barium, and strontium, such as chlorides, nitrates, etc., are dissolved in water, and the base precipitated as carbonate, with excess of ammonium carbonate and some free ammonia. The mixture is heated to about 60° C. for a few minutes. The precipitated carbonate is then to be filtered, well washed with hot water till all soluble matters, especially ammonia, are removed, and the precipitate with filter titrated with normal acid as already described.

Magnesium salts cannot be determined in this way.

(4) **Calcium and Magnesium Carbonates in Waters.**—The amount of calcium or calcium and magnesium carbonates dissolved in ordinary non-alkaline waters may be very readily, and with accuracy, found by taking 200 or 300 c.c. of the water, heating nearly to boiling, adding phenacetolin or lacmoid, and titrating cautiously with $^N/_{10}$ acid. An equally accurate result may be obtained by methyl orange in the cold liquid.

(5) **Determination of Calcium and Magnesium Sulphates, Chlorides, Nitrates, and Carbonates in Waters** and the degrees of hardness obtained without the use of Clark's Standard Soap Solution. As is generally known, the soap-destroying power of a water is ascertained in Clark's process by a standard solution of soap in weak alcohol, titrated against a standard solution of calcium chloride. The valuation is in so-called degrees, each degree being equal to 1 grain of calcium carbonate, or its equivalent, in the Imperial gallon. The process is an old and familiar one, but open to many objections from a scientific point of view. The scale of degrees is arbitrary, and is seriously interfered with by the presence of varying proportions of magnesium salts.

We are indebted, primarily to Mohr, and subsequently to

Hehner, for an ingenious method of determining both the temporary and permanent hardness of a water without the use of soap solution.

The standard solutions required are $^{N}/_{50}$ sodium carbonate and $^{N}/_{50}$ sulphuric acid. Each c.c. of standard acid exactly neutralizes 1 mgm. of $CaCO_3$ and each c.c. of the alkali precipitates the like amount of $CaCO_3$, or its equivalent in magnesium salts, in any given water.

METHOD OF PROCEDURE: 100 c.c. of the water are tinted with an indicator of suitable character, heated nearly to boiling, and standard acid cautiously added until the proper change of colour occurs. Hehner recommends phenacetolin; but my own experiments give the preference to lacmoid, which is also commended by Thomson. Draper* points out the value of lacmoid and carminic acid for such a process, and I fully endorse his opinion with respect to both indicators.

Another indicator, erythrosin, is recommended by J. W. Ellms†. The advantage this indicator possesses is that it is less affected by CO_2, the titration may be made in the cold, and it also gives more accurate results with fairly turbid or coloured water than with the indicators above mentioned. It is not, however, the preparation described on page 40, but is simply a sodium salt of erythrosin in ordinary use, dissolved in distilled water in the proportion of 0·1 gm. per litre. The titration is made in a 250 c.c. stoppered white bottle that it may be well shaken without loss. 100 c.c. of the water together with 2·5 c.c. of the indicator, and 5 c.c. of chloroform. These are well shaken and the acid added in small quantities, and well shaken after each addition. The rose colour of the water toward the end of the titration becomes less marked, and with a very slight excess of acid quite colourless. The chloroform produces a milky appearance from frequent shaking, but this is no hindrance to the end-point; if desired, however, it will settle in a short time. A piece of white paper behind the bottle will facilitate the detection of any trace of colour remaining as the titration approaches the end-point.

If the most accurate results are desired, any of the indicators should be submitted to a blank experiment by taking a measured volume of it with 100 c.c. of distilled water, and finding how much of the acid is required to remove the colour; the quantity of acid so found should then be deducted from all readings before converting them into calcium carbonate.

The number of c.c. of acid used represents the temporary hardness in parts per 100,000. To obtain "degrees of hardness," multiply the number of c.c. by 0·7. The permanent hardness is ascertained by taking 100 c.c. of the water and adding to it a rather large known excess of the standard sodium carbonate. The quantity must of course be regulated by the amount of sulphates, chlorides, or nitrates of calcium and magnesium present in the water; as a rule, a volume equal to that of the water will more than suffice. Evaporate in a platinum dish to dryness (glass or porcelain will not do, as they affect the hardness), then extract the soluble portion with small quantities of distilled water, pass through a very small filter, and titrate the filtrate with the standard acid for the excess of sodium carbonate: the difference represents the permanent hardness.

Some waters contain alkali carbonates, in which case there is of course no permanent hardness, because the salts to which this is due are decomposed by the alkali carbonate. In examining a water of this kind, the temporary hardness will be shown to be greater than it really is, owing to the alkali carbonate; and the experiment for permanent hardness will show more sodium carbonate than was actually added. If the difference so found is deducted from the temporary hardness, at first noted, the remainder will be the true temporary hardness.

* *C. N.* **51**, 206. † *J. Am. C. S.* 1899, p. 359.

AMMONIA.

$NH_3 = 17 \cdot 034$.

1. Determination of Combined Ammonia by distillation with Alkalies or Alkaline Earths.

THIS method brings about the expulsion of ammonia from all its salts. Caustic soda, potash, or lime may any of them be used. Where an organic nitrogenous compound exists in the substance it is in most cases necessary to submit it to preliminary treatment by Kjeldahl's method (p. 83).

There is a great variety of distilling vessels convenient for this process.

Any of the ordinary forms of apparatus will be found useful for accurately determining the ammonia in any of its compounds which can be decomposed by soda, potash, or lime. The gas so evolved is collected in a known volume in excess of standard acid, the excess of acid being afterwards found by residual titration with standard alkali. A compact modern form of apparatus is shown in fig. 28.

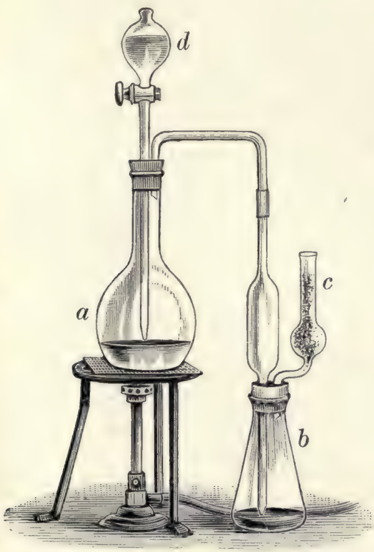


Fig. 28.

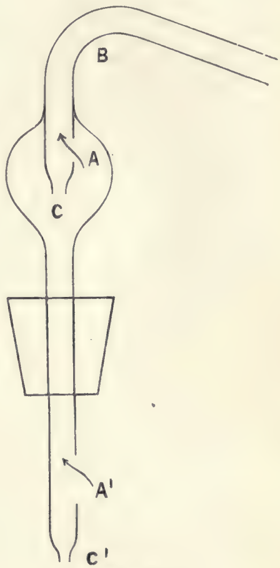


Fig. 29.

An ingenious and useful distillation tube for rapid determinations of ammonia designed by Hopkins* is shown in fig. 29. It is made from tubing of 7 to 8 mm. bore. The side openings, A and A_1, should be nearly as large, and the bulb about 5 cm. in

* *J. Am. C. S.* 1896, p. 227.

diameter. The length of the tube below the bulb is 12 cm., and that above the bulb about the same. The jets C and C_1 are 2 mm. inside diameter. In use, the tube is pushed through the cork of the distilling flask until the opening A_1 is below the cork; the vapour then passes through the side openings, and whatever condenses in the tube below the bend B, runs back into the flask through the jets C and C_1, which always remain filled with liquid.

METHOD OF PROCEDURE: The distilling flask *a* (see Fig. 28), capacity about 400 c.c., is placed upon the wire gauze, and contains the ammoniacal substance. The tube *d* is filled with strong caustic potash or soda. The flask *b* holds about 300 c.c. and contains a measured quantity of standard acid, part being contained in the tube *c* which is filled with glass wool or broken glass, and through which the standard acid has been poured. The stoppers of the flasks should be of caoutchouc, failing which, good corks soaked in melted paraffin may be used.

The substance to be examined is weighed or measured, and put into the distilling flask *a* with a little water. The apparatus then being made tight at every point, some of the caustic alkali is allowed to flow into *a* by opening the tap of *d*, and the gas or spirit lamp is lighted under it.

The contents are brought to gentle boiling, taking care that the froth, if any, does not enter the distilling tube. It is as well to use a movable gas burner or common spirit lamp, so that, if there is any tendency to boil over, the heat can be removed immediately and the flask blown upon by the breath, which reduces the pressure in a moment. In examining guano and other substances containing ammoniacal salts and organic matter the tendency to frothing is considerable, and unless the above precautions are taken the accuracy of the results will be interfered with. A small piece of beeswax, solid paraffin, or granulated zinc is very serviceable in preventing frothing or bumping.

The distilling tube has both ends cut obliquely, and the lower end nearly, but not quite, reaches to the surface of the acid, to which a little methyl orange may be added. The quantity of standard acid used must, of course, be more than sufficient to combine with the ammonia produced; the excess is afterwards ascertained by titration with standard alkali. The boiling should be continued till about two-thirds of the liquor in the distilling flask have distilled over. The tube *c* must be thoroughly washed out into the flask *b* with distilled water, so as to carry down the acid with any combined gas which may have reached it. The titration then proceeds as usual. Each c.c. of $^N/_1$ acid neutralized by the ammonia $=0{\cdot}017$ gram. of NH_3.

2. Indirect Method.

In the case of tolerably pure ammoniacal salts or liquids free from acid, or in which the free acid has previously been determined, a simple indirect method can be used, as follows:—

If the ammoniacal salt be boiled in an open vessel with normal caustic alkali the ammonia is entirely set free, leaving its acid combined with the fixed alkali. If, therefore, the quantity of alkaline solution is known, the excess beyond that necessary to replace the ammonia may be found by titration with normal acid. The boiling of the mixture must be continued till a piece of red litmus paper, held in the steam from the flask, is no longer turned blue.

EXAMPLE: 5 grams of a dirty sample of sulphate of ammonia were boiled on a sand-bath in a large flask with 100 c.c. of $^N/_1$ NaOH till all ammonia was expelled. On then titrating back with Normal H_2SO_4 29·4 c.c. were required. The free acid in 5 grams required 1·2 c.c. of $^N/_1$ NaHO. Hence $100-1{\cdot}2-29{\cdot}4=69{\cdot}4$, and $\cdot 017\times 69{\cdot}4\times 20=23{\cdot}59\ \%\ NH_3$.

3. Technical Analysis of Ammoniacal Gas Liquor, Sulphate of Ammonia, Sal Ammoniac, etc. (arranged for the use of Manufacturers).

This process depends upon the fact that when ammoniacal salts are boiled with caustic soda, potash, or lime, the whole of the ammonia is expelled in a free state and may by a suitable apparatus (fig. 28) be determined with extreme accuracy (see p. 76).

Technical Analysis of Gas Liquor.—This liquid consists of a solution of carbonates, sulphates, hyposulphites, sulphides, sulphocyanides, and other salts of ammonia. The object of the ammonia manufacturer is to get all these out of his liquor into the form of sulphate or chloride as economically as possible. The whole of the ammonia existing free or as carbonate in the liquor can be distilled off at a steam heat; the fixed salts, however, require to be heated with soda, potash, or lime (the latter is generally used on a large scale as being most economical, sometimes with an addition of caustic soda towards the end of the distillation), in order to liberate the ammonia contained in them.

The apparatus here described is the same on a small scale as is necessary in the actual manufacture of sulphate of ammonia in quantities; and its use enables any manufacturer to tell to a fraction how much sulphate of ammonia he ought to obtain from any given quantity of gas liquor. It also enables him to tell exactly how much ammonia can be distilled off with heat alone, and how much exists in a fixed condition requiring lime or caustic soda.

The measures used in this process are on the metric system, the use of which may, perhaps, at first sight appear strange to English manufacturers; but as the only object of the process is to obtain the percentage of ammonia in any given substance, it is a matter of no importance which system of measures or weights is used, as when once the percentage is obtained the tables will show the result in English terms of weight or measure.

Method of Procedure: Whatever the strength of the liquor 10 c.c., measured by a pipette, is the quantity invariably used for the analysis. This quantity is transferred without spilling a drop to the distilling flask—the fittings having been previously removed—and the tube *d* (Fig. 28) is then filled with strong caustic soda solution. The cork is then replaced, and the flask securely imbedded in perfectly dry sand in a sand-bath or supported on wire gauze. 20, 30, 40 or 50 c.c. of standard acid—according to the estimated strength of the liquor—are allowed to flow into the receiving flask through the tube *c* (Fig. 28), which is filled with broken glass placed on a layer of glass wool or fibrous asbestos. The broken glass should be completely wetted with the acid, so that any vapours of ammonia which may escape the acid in the flask shall become absorbed by the acid. The quantity of standard acid to be used is regulated by the approximately known strength of the liquor, which of course can be told by Twaddle's hydrometer: thus for a liquor of 3° Twaddle (=6-oz. liquor), 20 c.c.—8-oz., 25 c.c.—10-oz., 30 c.c. of acid will be sufficient—but there must always be an excess. The required quantity can always be approximately known, since every 10 c.c. of acid represents 1 per cent. of ammonia. The standard acid having been carefully passed through c (Fig. 28), the apparatus is fitted together by the elastic tube and the india-rubber stoppers

securely inserted in both flasks; this being done, the lamp is lighted under the sand-bath, and at the same time the tap on *d* (Fig. 28) is opened, so as to allow caustic soda to flow into the distilling flask. The heat is continued to boiling, and allowed to go on till the greater bulk of the liquid has distilled over into the receiving flask. A quarter of an hour is generally sufficient for this purpose, but if the boiling is continued till the liquid just covers the bottom of the flask, all the ammonia will have gone over; during the whole operation the distilling tube must never dip into the acid in the receiving flask. The apparatus may then be detached; distilled or good boiled drinking water is then poured repeatedly through the tubes in small quantities, till all traces of acid are washed down into the receiving flask. This latter now contains all the ammonia out of the sample of liquor, with an excess of acid, and it is necessary now to find out the quantity of acid in excess. This is done by means of a standard solution of caustic soda, which is of exactly the same strength as the standard acid. In order to determine the amount of the standard acid which has been neutralized by the ammonia distilled from the liquor we first cool the receiving flask containing the distillate, add to it one drop of methyl orange or a sufficiency of some other suitable indicator (but not phenolphthalein), and cautiously run into it from a burette the standard caustic soda solution, with constant shaking, until the indicator changes colour. The number of c.c. of soda so used, deducted from the number of c.c. of standard acid originally taken, gives the number of the latter neutralized by the ammonia in the distillate and hence in the 10 c.c. of gas liquor distilled. The strengths of the standard solutions used are such that the result required is obtained without any calculation.

EXAMPLE: Suppose that a liquor is to be examined which marks 5° Twaddle, equal to 10-oz. liquor; 10 c.c. of it are distilled into 30 c.c. of the standard acid, and it has afterwards required 6 c.c. of standard soda to neutralize it; this leaves 24 c.c. as the volume of acid saturated by the distilled ammonia, and this represents 2·4 per cent.; and on referring to the table it is found that this number corresponds to a trifle more than 11 ounces, the actual figures being 2·384 per cent. for 11-ounce strength.

The strength of the standard soda and acid solutions is so arranged that when 10 c.c. of liquor are distilled every 10 c.c. of acid solution represents 1 per cent. of ammonia in the liquor. Thus, 13 c.c. of acid will represent 1·3 per cent. of ammonia, corresponding to 6-ounce liquor.

The burette is divided into tenths of a cubic-centimetre, and those who are familiar with decimal calculations can work out the results to the utmost point of accuracy; the calculation being that every 1 per cent. of ammonia requires 4·61 ounces of concentrated oil of vitriol (sp. gr. 1·845) per gallon of liquor, to convert it into sulphate. Thus, suppose that 10 c.c. of any given liquor have been distilled, and the quantity of acid required amounts to 18·6 c.c., this is 1·86 per cent., and the ounce strength is $4{\cdot}61 \times 1{\cdot}86 = 8{\cdot}5746$. The liquor is therefore a trifle over 8½-ounce strength.

Spent Liquors.—It is frequently necessary to ascertain the percentage of ammonia in spent liquors in order to see if the workmen have extracted all the available ammonia. In this case the same measure, 10 c.c. of the spent liquor, is taken, and the operation conducted precisely as in the case of a gas liquor.

EXAMPLE: 10 c.c. of a spent liquor were distilled, and found to neutralize 3 c.c. of acid: this represents three-tenths of a per-cent. equal to 1-oz. and four-tenths of an ounce, or nearly 1½ oz. Such a liquor is too valuable to throw away, and should be worked longer to extract more ammonia.

METHOD OF PROCEDURE FOR SULPHATE OF AMMONIA OR SAL AMMONIAC: An average sample of the salt being drawn, ten grams are weighed, transferred without loss to a 100 c.c. flask, distilled or boiled drinking water poured on it, and well stirred till disolved, and finally water added exactly to the mark. The 10 c.c. measure is then filled with the solution, and emptied into the distilling flask; 30 c.c. of standard acid are put into the receiving flask and the distillation carried on precisely as in the case of the gas liquor. The number of c.c. of standard acid required shows directly the percentage of ammonia; thus if 24·6 c.c. are used in the case of sulphate, it contains 24·6 per cent. of ammonia.

The liquors when tested must be measured at ordinary temperatures, say as near 60° F. as possible. The standard solutions must be kept closely stoppered and in a cool place.

The following table is given to avoid calculations; of course, it will be understood that the figures given are on the assumption that the whole of the ammonia contained in the liquor is extracted in the manufacture as closely as it is in the experiment. With the most perfect arrangement of plant, however, this does not as a rule take place; but it ought to be very near the mark with proper apparatus, and care on the part of workmen.

Approximate measure of Standard Acid in c.c. and tenths.	Percentage of Ammonia NH_3.	Ounce strength per gallon.	Weight of Sulphuric Acid in pounds and decimal parts required for each gallon of liquor.			Yield of Sulphate per gallon in lb. and decimal parts.
			C. O. V. 169° Tw.	B. O. V. 144° Tw.	Chamber Acid 120° Tw.	
2·2	·2168	1	·0625	·0781	·0893	·0841
4·3	·4336	2	·1250	·1562	·1786	·1682
6·5	·6504	3	·1875	·2343	·2679	·2523
8·7	·8672	4	·2500	·3124	·3572	·3364
10·1	1·0840	5	·3125	·3905	·4465	·4205
13·0	1·3000	6	·3750	·4686	·5358	·5046
15 2	1·5176	7	·4375	·5467	·6251	·5887
17·3	1·7344	8	·5000	·6248	·7144	·6728
19·5	1·9512	9	·5625	·7029	·8037	·7569
21·7	2·1680	10	·6250	·7810	·8930	·8410
23·8	2·3840	11	·6875	·8591	·9823	·9251
26·0	2·6016	12	·7500	·9372	1·0716	1·0092
28·2	2·8184	13	·8125	1·0153	1·1609	1·0933
30·4	3·0350	14	·8750	1·0934	1·2502	1·1774
32·5	3·2520	15	·9375	1·1715	1·3395	1·2615
34·7	3·4688	16	1·0000	1·2496	1·4288	1·3456
36·9	3·6856	17	1·0625	1·3277	1·5181	1·4297
39·0	3·9024	18	1·1250	1·4058	1·6074	1·5138
41·2	4·1192	19	1·1875	1·4839	1·6967	1·5979
43·3	4·3360	20	1·2500	1·5620	1·7860	1·6820

The weight of sulphuric acid being given in decimals renders it very easy to arrive at the weight necessary for every thousand gallons of liquor, by simply moving the decimal point; thus 8-oz. liquor would require 500 lb. of concentrated oil of vitrol, 625 lb. of brown oil of vitriol, or 714½ lb. chamber acid for every 1000 gallons, and should yield in all cases 672·8 (say 673) lb. of sulphate.

4. Technically complete analysis of Ammoniacal Liquors.

The Annual Reports of the Chief Inspector under the Alkali, etc. Works Regulation Act have for some years past recorded the results of investigations conducted in his laboratory on ammoniacal liquors from various sources. The last edition of this work contained a general summary of the analytical methods adopted, as given in the Report for 1903. Since that date the procedure there recommended has been modified as the result of further study and research in the Chief Inspector's laboratory and elsewhere, notably by Feld*, and Mayer and Hempel†.

The procedure now approved is the following ‡ :—

METHODS OF ANALYSIS.—1. *Free Ammonia.* (*a*) By direct titration, to determine approximately the volume of acid required for distillation (*b*):—10 c.c. of liquor are diluted to 100 c.c. and titrated with $^N/_2$ H_2SO_4, Methyl orange indicator.

(*b*) By distillation:—10 c.c. of liquor (more if weak) are diluted to about 300 c.c. in a round-bottomed flask connected through a catch bulb to Liebig condenser and receiver containing excess of $^N/_2$ H_2SO_4 and provided with outlet acid catch packed with broken Jena glass (some beads are found to yield alkali to $^N/_2$ acid, and their use is not recommended). 150 c.c. of the solution are distilled over and the excess of acid in the receiver is titrated with $^N/_2$ Na_2CO_3. On further distillation certain liquors continue to evolve small traces of ammonia. The presence of this ammonia is attributed to the slow decomposition of nitrogenous bodies, and the distillation for free ammonia is therefore not continued beyond 150 c.c.

2. *Fixed Ammonia.* By distillation:—Add 100 c.c. of half-normal caustic soda solution to the residual liquor in flask (*b*) above, and proceed as before.

$$NH_3\text{, grams per 100 c.c. of liquor} = \cdot 0085 \times 10 \times \text{c.c. } ^N/_2 \text{ acid.}$$

$$\text{H.E.§ ("Hydrogen equivalent")} = \frac{\text{Free } NH_3\text{, grams.}}{\cdot 017}$$

3. *Carbonic Acid.* 10 c.c. of liquor (more, if dilute) are diluted to 400 c.c. in a suitable flask provided with a Bunsen rubber valve; 10 c.c. of ammoniacal calcium chloride (1 c.c. = ·044 gram CO_2) are added and the whole heated for 1½ to 2 hours in a water bath at 100° C. The calcium carbonate obtained by filtration is washed back into the flask, dissolved in $^N/_2$ HCl, and the excess of acid titrated with $^N/_2$ Na_2CO_3. The small amount of calcium carbonate left on the filter paper is best recovered by incineration and added to the contents of the flask.

$$CO_2\text{, grams per 100 c.c. of liquor} = \cdot 011 \times 10 \times \text{c.c. } ^N/_2 \text{ acid.}$$

$$\text{H.E.} = \frac{CO_2\text{, grams}}{\cdot 022}$$

4. *Chloride.* 10 c.c. of boiled liquor are diluted to 150 c.c., 25 c.c. of hydrogen peroxide (10 vols. "free from chloride")|| added, and the whole boiled for 15 minutes to oxidize thiocyanate, &c. To the hot solution are added five or six drops of a 10 per cent. solution of potassium chromate and the boiling continued for two minutes, then a slight excess of sodium carbonate with boiling for one minute. The solution, which should possess a clear lemon colour, is filtered, cooled, and made up to 250 c.c.; an aliquot portion is then titrated with $^N/_{10}$

* *J. S. C. I.* 1903, p. 1068. † *Jour. für Gasbeleuchtung*, 1908.

‡ I am indebted to Mr. E. Linder, Assistant to the Chief Inspector, for an advance proof of his Memorandum as it appears in the Annual Report for 1909.

§ NOTE.—For method of stating result, see paper by Lewis T. Wright, *Journ. Soc. Chem. Ind.* 1886, pp. 655-661; also Appendix, Annual Report, 1905, p. 48, example of analysis of typical gas liquor with calculation of results.

|| Some chemists prefer to use Merck's perhydrol, a reagent free from chloride.

$AgNO_3$ (potassium chromate indicator) after neutralizing with dilute nitric acid. A blank experiment is made with 10 c.c. of $^N/_{10}$ NaCl, and the same volumes of water, peroxide, and chromate as in the actual analysis, to determine the correction for traces of chloride in the reagents used. Should the organic matter in solution resist oxidation, further addition of peroxide must be made and the boiling continued, with addition of potassium chromate as before.

$$\text{HCl, grams per 100 c.c.} = \cdot 00364 \times 10 \times \text{c.c. } ^N/_{10}\ AgNO_3.$$

5. *Sulphur.* (*a*) As sulphate :—250 c.c. of the liquor are concentrated to about 10 c.c. on the water bath, 2 c.c. of strong hydrochloric acid added, and the evaporation continued to dryness to decompose thiosulphate and render organic matter less soluble. The residue is extracted with water, and the filtered solution made up to 250 c.c. ; 100 c.c. of this solution are acidified with hydrochloric acid, brought to the boil, and barium chloride added ; the precipitate, after standing one night, is filtered and weighed.

$$\text{Sulphur as sulphate, grams per 100 c.c.} = 0 \cdot 1373 \times \text{grams } BaSO_4.$$

(*b*) As sulphide, sulphite, and thiosulphate.

10 c.c. of liquor are diluted to 500 c.c., acidified with hydrochloric acid and titrated with $^N/_{10}$ iodine, the flask being closed and well shaken at the end of the titration to re-absorb sulphuretted hydrogen gas above the solution. The volume of $^N/_{10}$ iodine required determines that of the liquor taken. Thus,

10 c.c. of liquor (or more) are run into excess of $^N/_5$ ammoniacal zinc chloride solution diluted to about 80 c.c. ; the solution is warmed to coagulate the sulphide, filtered, and the precipitate washed with water at 40° to 50° C.

(i) Sulphide.—The zinc sulphide on the filter is washed into excess of $^N/_{10}$ iodine acidified with hydrochloric acid (the last traces of sulphide being washed through with cold dilute acid). After vigorous shaking to complete the solution of the sulphide (an important point to attend to), the excess of iodine is determined with $^N/_{10}$ thiosulphate,—starch indicator.

$$\text{Sulphur as sulphide, grams per 100 c.c.} = 10 \times \cdot 0016 \times \text{c.c. } ^N/_{10} \text{ iodine.}$$
$$\text{Sulphuretted hydrogen,} \quad ,, \quad = 10 \times \cdot 0017 \times \text{c.c. } ^N/_{10} \text{ iodine.}$$
$$\text{"H.E."} = \frac{H_2S,\ \text{grams.}}{\cdot 017}$$

(ii) Sulphite and Thiosulphate.—An approximate method for the differentiation of sulphite and thiosulphate was described in Annual Report, 1903, p. 36.* Mayer and Hempel† describe a method based upon the use of strontium chloride, which they consider to be sufficiently accurate for the desired purpose. Prolonged experience in the analysis of ammoniacal liquors, however, has led the author to the conclusion that no exact estimation of sulphite and thiosulphate is possible in such liquors by any method based on titration with iodine, save in quite exceptional cases, and he prefers to present a *united* figure for sulphur as sulphite and thiosulphate, reached by "difference": by subtracting from the "total sulphur" found by bromine oxidation the sulphur present in the form of sulphate, thiocyanate, and sulphide.

(*c*) *Sulphur as Thiocyanate.* (i) Ferrocyanide absent. 50 c.c. of the solution are treated with lead carbonate to remove sulphide, the lead sulphide and carbonate are then removed by filtration and thoroughly washed ; to the filtrate acid sulphite of soda, containing a little free SO_2, is then added, followed by distinct excess of a 10 per cent. solution of copper sulphate, and the solution allowed to stand for 5 to 10 minutes at 70° to 80° C. to coagulate the cuprous thiocyanate. The solution is then filtered and thoroughly washed with boiling water until the final washings remain colourless on addition of dilute potassium ferrocyanide; the residue on the filter is then washed back into the flask, digested at 30° to 40° C. with 25 c.c. of a 4 per cent. solution of caustic soda (free from chloride) and filtered. To the cold filtrate are added 5 c.c. of nitric acid free from oxides of nitrogen (50 per cent. strength) followed by 1 c.c. of a saturated solution of iron alum ; the solution is then filtered, if necessary, from separated organic matter, and titrated with $^N/_{10}$ $AgNO_3$.

* See *Polysulphide Method.* Vol. Anal., 9th edition, p. 80.

† *J. für Gasbeleuchtung*, 1908.

Sulphur as thiocyanate, grams per 100 c.c. $=2 \times \cdot 0032 \times$ c.c. $^{N}/_{10}$ $AgNO_3$.
Hydrocyanic acid as thiocyanate, ,, $=2 \times \cdot 0027 \times$ c.c. $^{N}/_{10}$ $AgNO_3$.

(ii) Ferrocyanide present.—50 c.c. of the liquor are slightly acidified with sulphuric acid, and ferric alum solution added in sufficient quantity to impart a decided red coloration ; the solution is now warmed to 60° C., filtered from the Prussian blue, and washed with water containing sodium sulphate. The filtrate is then treated as in (i) above.

(*d*) *Total Sulphur.*—50 c.c. of liquor (100 c.c. if weak) are slowly dropped into a flask containing excess of bromine (free from sulphur) covered by water moderately acidified with hydrochloric acid. The oxidized solution is evaporated to dryness on the water bath, the residue extracted with boiling water, filtered, cooled, made up to 250 c.c. and 100 c.c. precipitated with barium chloride in the usual way.

Sulphur, grams per 100 c.c. $=5 \times \cdot 1373 \times$ grams $BaSO_4$.

In the case of certain liquors, *e.g.*, coke and blast furnace liquors, oxidation with bromine yields a heavy yellow precipitate of brominated phenols ; this precipitate may retain traces of sulphate in amount sufficient to affect the percentage distribution figures unless it is recovered by fusion with the smallest quantity of potassium carbonate and nitrate, or sodium peroxide, and included in the total.

6. *Ferrocyanide*, by Feld's method*. Mayer and Hempel take 250 c.c. of liquor, acidify slightly with sulphuric acid, and add ferric alum solution in sufficient excess to impart a deep red coloration (ferric thiocyanate). The solution is then heated to 60° C. and filtered. Should the filtrate be coloured blue, it must be returned to the filter and the process repeated until a small quantity shows no blue colour after addition of mercuric chloride to destroy the ferric thiocyanate. The precipitate is then washed two or three times with water containing sodium sulphate. Filter and precipitate are next transferred to a flask and the Prussian blue decomposed by boiling for 5 minutes with 10 c.c. of normal caustic soda, and the solution diluted to 150 c.c.; 15 c.c. of magnesium chloride solution (610 grams $MgCl_2$ $6H_2O$ per litre) are next added to the boiling solution very slowly and with constant agitation to avoid the formation of clots of magnesium hydroxide. To the boiling mixture about 100 c.c. of boiling mercuric chloride solution (27.1 grams $HgCl_2$ per litre) are added, and the whole is boiled from 5 to 15 minutes. The liquor is then distilled for 20 to 30 minutes with addition of 30 c.c. of sulphuric acid (196 grams H_2SO_4 per litre), the hydrocyanic acid being collected in 25 c.c. of normal caustic soda and titrated as described in the method for estimation of hydrocyanic acid below.

1 c.c. $AgNO_3 00 = \cdot 54$ gram HCy.
$= \cdot 00947$ gram $(NH_4)_4FeCy_6$.

7. *Hydrocyanic Acid*, by Feld's method. 50 c.c. of liquor are distilled with excess of a saturated solution of lead nitrate.

The apparatus employed is similar to that used for estimation of ammonia and ferrocyanide. It consists of a 500 c.c. round-bottomed flask provided with two-holed caoutchouc stopper with inlet tube sealed in liquor and exit tube connected through a catch bulb to Liebig condenser and receiver. The exit tube of the condenser is sealed in the 25 c.c. of normal soda with which the receiver is charged, residual gases escaping through a scrubbing bulb containing broken glass moistened with caustic soda. At the end of the distillation a current of air is drawn through the apparatus for a few minutes as a necessary precaution. The distillate is diluted to 400 c.c., a crystal of potassium iodide added, and the solution titrated on $^{N}/_{10}$ $AgNO_3$.

HCy, grams per 100 c.c. $=2 \times \cdot 0054 \times$ c.c. $^{N}/_{10}$ $AgNO_3$.

$$\text{“H.E.”} = \frac{\text{HCy, grams.}}{\cdot 027}$$

* Dr. Skirrow (*Journ. Soc. Chem. Ind.*, 1910, p. 319) has recently questioned the accuracy of Feld's method for determination of ferrocyanide, but his conclusions are challenged by Dr. Colman (*Analyst*, 1910, 35, 295,).

Certain ammoniacal liquors, *e.g.*, coke oven liquors, froth considerably on distillation with lead nitrate, the flask, therefore, should be heated cautiously. In general, the distillation will be complete when 100 c.c. of liquor have passed over (30 to 40 minutes gentle boiling).

(8) *Phenols.*—No occasion has yet arisen to determine the amount of phenols present in ammoniacal liquors. A very suitable method for their estimation is that described by Dr. F. W. Skirrow (*Jour, Soc. Chem. Ind.*, 1908, p. 58). The phenol is distilled off with water and then converted into tri-iodophenol by means of excess of iodine, which is titrated back with thiosulphate.

5. Determination of Combined Nitrogen in Organic Substances.

The old process consists in heating the dried substance in a combustion tube with soda lime, by which the nitrogen is converted into ammonia ; and this latter, being led into a measured volume of standard acid contained in a suitable bulb apparatus, combines with its equivalent quantity ; the solution is then titrated residually with standard alkali for the excess of acid, and thus the quantity of ammonia found.

As the combustion tube with its arrangements for organic analysis is well known and described in any of the standard books on general analysis, it is not necessary to give a description here.

6. Kjeldahl's Method and its developments.

This has met with considerable acceptance in lieu of the combustion method, on account of its easy management and accurate results. Unlike the combustion method, the ammonia is obtained free from organic matters and colour, and moreover salts of ammonia and nitrates may be determined with extreme accuracy. It was first described by Kjeldahl*, and has since been commented upon by many operators, among whom are Warington**, Pfeiffer and Lehmann†, Marcker and others‡; Gunning§; Arnold and Wedermeyer‖; and Bernard Dyer¶.

The original process consisted in heating the nitrogenous substance in a flask with concentrated sulphuric acid at boiling temperature, and, when the oxidation through the agency of the acid is nearly completed, adding finely powdered potassium permanganate in small quantities till a green or pink colour remains constant (long experience has shown that this addition of permanganate is not advisable, as it leads to loss of ammonia) ; the whole of the nitrogen is thus converted into ammonium sulphate. The flask is then allowed to cool, diluted with water, excess of caustic soda added, the ammonia distilled off into standard acid, and the amount found by titration in the usual way.

Some practical difficulties occurred in the process as originally devised ; moreover, with some organic substances a very long time was required to oxidize the carbon set free by the strong acid.

Another difficulty was that if nitrates were present in the com-

* *Z. a. C.* **22**, 366. ** *C. N.* **52**, 162. † *Z. a. C.* **24**, 388. ‡ *Z. a. C.* **23**, 553 ; **24**, 199, 393 ; **25**, 149, 155 ; **26**, 92 ; **27**, 222, 398. § *Ibid* **28**, 188. ‖ *Ibid* **31**, 525. ¶ *J. C. S.* 1895, 811.

pound analyzed their reduction to ammonia was neither certain nor regular, and unless this difficulty could be overcome the value of the process was limited.

The various modifications of the original process are as follows :—

Gunning proposed the addition of potassium sulphate to the sulphuric acid, by which means its boiling point is raised and the process of oxidation greatly facilitated. Arnold proposed the use of mercury, as affording still further assistance in the same direction. Jodlbauer proposed the use of a mixture of phenol or, better, salicylic acid and sulphuric acid for use with substances containing nitrates as well as organic or ammoniacal nitrogen.

The experience of these and many hundreds of other operators since this method was first introduced has resulted in rendering it as perfect as need be, and the results of this experience in all essential particulars will now be described, omitting the details as to some of the special forms of apparatus which are not absolutely essential. The method requires the following re-agents and apparatus :—

1. Standard acid, which may be either sulphuric or hydrochloric ; a convenient strength is semi-normal or fifth-normal.

2. Standard alkali, either ammonia, or sodium or potassium hydroxide, of corresponding strength to the acid.

3. Concentrated sulphuric acid free from nitrates and ammonium sulphate.*

4. Mercuric oxide prepared in the wet way or metallic mercury.†

5. Powdered potassium sulphate.

6. Granulated zinc.

7. Solution of potassium sulphide in water, 40 gm. in the litre.

8. A saturated solution of caustic soda free from nitrates or nitrites. This should be tried as to the amount required to saturate 20 c.c. of the sulphuric acid (3 above) used and marked on the stock bottle. About 5—10 c.c. more than this amount is added to the distillation flask for each 20 c.c. of acid used.

9. An indicator—litmus, methyl orange, or cochineal are suitable, but phenolphthalein may not be used.

10. Digestion flasks with long neck and round bottom, holding about 200—250 c.c. These flasks should be well annealed, and not

* Commercial oil of vitriol frequently contains ammonium compounds, owing to the fact that makers sometimes add ammonium sulphate during concentration in order to get rid of nitrous compounds. Meldola and Moritz state that any traces of ammonia may be destroyed by digesting the acid for two or three hours at a temperature below boiling with sodium or potassium nitrate in the proportion of 0·5 gm. of the salt to 100 c.c. of acid. Lunge objected to this treatment, because of the probable formation of nitro-sulphuric acid. Experiments have since been made by Moritz which prove that the objection is groundless, provided the digestion is carried on for a period sufficient to expel the nitrous acid (*J. S. C. I.* **9**, 443). The purification of the acid may of course be obviated by ascertaining once for all the amount of ammonia in any given stock of acid, by making a blank experiment with pure sugar and allowing in all cases for the amount of NH_3 so found.

† C. A. Mooers (*Analyst* **28**, 44) states that when using mercury with the material under examination, there is a danger of the metal passing over with the distillate and forms an amalgam with the tin condensing tubes which absorbs some of the ammonia. He therefore advocates Jena glass instead of tin tubes. No such effects have been obtained in my laboratory with the apparatus fig. 31. It is possible that the danger alluded to is due to impure tin or to the form of distilling flask used.

too thick, preferably made of Jena glass—the neck about ¾ inch wide, and 3½—4 inches long.

11. Distillation flasks of hard Bohemian or Jena glass of conical shape, 600-850 c.c. capacity, fitted with a rubber stopper and a bulb above with curved delivery tube, to prevent the spray of the boiling alkaline liquid from being carried over into the condenser tubes. Copper distilling bottles or flasks are used by some operators for technical purposes with good results, but in this case it is advisable to put the soda into the vessel first, then to add the acid liquid.

12. The condenser. Owing to the undoubted solubility of glass in freshly distilled water containing ammonia, it is advisable to have the condenser tube made of pure block tin. This should be about three-eighths of an inch wide externally, and is connected with the bulb tube of the distilling flask with stout pure rubber tube. It is surrounded by either a metal or glass casing, through which a current of cold water is passed in the usual manner. It is very easy to fit up such an arrangement with the condenser tubes made entirely of glass sold by the dealers in chemical apparatus. The end of the condenser tube may be simply inserted into the neck of a flask containing the standard acid, or it may have a delivery tube connected by a rubber tube leading into a beaker. There is no necessity for dipping the delivery tube into the acid unless the temperature of the laboratory is very high.

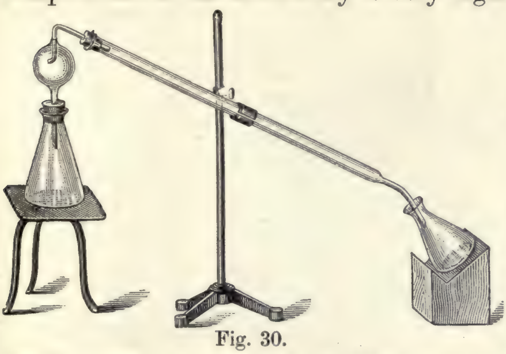


Fig. 30.

In places where it is difficult to arrange for a flow of water to keep the distilling tube cool the simple apparatus shown in fig. 30 may be serviceable, and unless the temperature of the laboratory is exceedingly high there is no loss of ammonia. This arrangement is used by Stutzer, whose results with it compare well with others made with condensers surrounded by flowing water. The explanation of this is, no doubt, that ammonia possesses a very strong affinity for water and, when in very minute quantity, is held tenaciously even at a tolerably high temperature. The tube should be not less than 3 feet long. Where a large number of determinations are being carried on it is convenient to have a special condenser, which will allow of six or more distillations being worked at the same time. Several forms of such arrangements have been devised, and are obtainable from apparatus dealers.

For use in my own laboratory, where a large number of agricultural samples are examined, the form shown in fig. 31 has been adopted and has been found to answer well. The body of the condenser

consists of an ordinary 10-gallon iron drum filled with water; the pure tin distilling tubes run through this at equal distances from each other, and emerge at the bottom of sufficient length to dip into the vessels containing the standard acid. With this arrangement there is no necessity for running water, and six distillations may be carried on simultaneously without fear of losing ammonia; the body of water is so great that the lower portion is quite cool after the distillations are finished. In case of extremely hot weather or in a very hot laboratory the cover may be removed and a lump of ice placed in the water if a large number of distillations are required.

The distilling flasks are closed with rubber stoppers, and fitted with glass bulb tops as in figs. 30 and 31. These are connected with the tin tubes by rubber joints, and supported on an iron frame over which is laid a strip of wire gauze. The Bunsen burners are of Fletcher's make, with nickel gauze tops which give a smokeless flame of any desired size. So well does this arrangement work that during many hundreds of distillations not one breakage has occurred due to the heating or the distillation. The tin condensing tubes do not in this case dip into the standard acid, as various

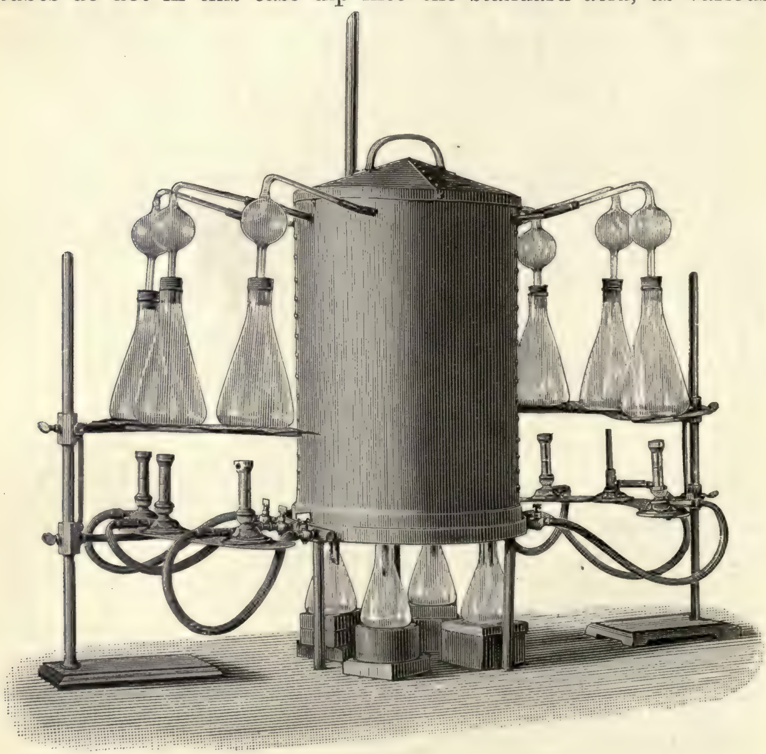


Fig. 31.

experiments have proved it unnecessary unless the temperature of the laboratory is very high.

B. Dyer uses a tin condensing tube (air condenser) rising 15—18 inches vertically from the distilling flask, then bent downwards and fitting into a pear-shaped adapter (with large expansion to allow of varied pressure), whose narrowed end dips actually into the acid. The receiving flask should stand in a tank of running water.

13. A convenient stand for holding the digestion flasks is shown in fig. 32. They rest in an oblique position and heat is applied by small Bunsen burners. With a little care the naked flame can be applied directly to the flask without danger. Some operators prefer to close the digestion flasks with a loosely fitting glass stopper elongated to a point, and having a balloon-shaped top. This aids in the condensation of any acid which may distil, but if the flasks are tolerably long in the neck, there is practically no loss of acid except as SO_2 which occurs in any case. It is almost needless to say that the digestion should be done in a fume closet with good draught.

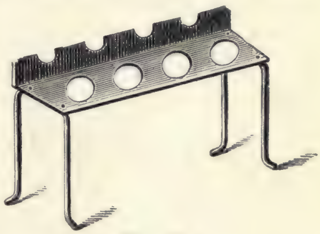


Fig. 32.

As the acid fumes given off when organic matters are boiled with strong acid are very disagreeable and irritating to the lungs, especially in small laboratories, another method can be adopted so that no fume closet is necessary, and the digestion can be carried on in the open air. The acid flask is closed with a pear-shaped hollow stopper, attached to which is a bent glass tube, the end of which is passed through a cork into a globe-shaped adapter held in the neck of a conical flask, which contains a solution of caustic soda into which the end of the adapter dips. By this method all the acid fumes are absorbed.*

Determination of Nitrogen in the absence of Nitrates.

The Kjeldahl-Gunning Process: From 0·5 to 5 gm. of the substance according to its nature is brought into a digestion flask with approximately 0·5 gm. of mercuric oxide or a small globule of the metal and 20 c.c. of sulphuric acid (in case of bulky vegetable substances 30 c.c. or more may be necessary). The flask is placed on wire gauze over a small Bunsen burner in an upright position, or in the frame above described in an inclined position, and heated below the boiling-point of the acid for from five to fifteen minutes, or until frothing has ceased. The heat is then raised till the acid boils briskly, and the boiling continued for about fifteen minutes, when about 10 grams of potassium sulphate are added and the boiling resumed. Anhydrous sodium sulphate also answers this purpose, and the same effect can be obtained in the same time by sodium pyrophosphate, 2 gm. of the latter acting as well as 10 gm. of either of the former. No further attention is required till the contents of the flask have become a clear liquid, which is colourless, or at least has only a very pale straw colour. The flask is then removed from the frame, and, after cooling, the contents are transferred to the distilling flask with repeated quantities of water amounting

* A figure of this apparatus is shown in *Analyst* **28**, 54.

in all to about 250 c.c., and to this 25 c.c. of potassium sulphide solution are added, soda solution* sufficient in quantity to make the reaction strongly alkaline, and a few pieces of granulated zinc. The flask is at once connected with the condenser, and the contents are distilled till all ammonia has passed over into the standard acid, and the concentrated solution can no longer be safely boiled. This operation usually requires from twenty to thirty minutes. The distillate is then titrated with semi-normal or fifth-normal alkali.

The use of mercury or its oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour, and in the case of substances most difficult to oxidize is more commonly less than an hour. Potassium sulphide removes all mercury from solution, and so prevents the formation of mercuro-ammonium compounds which are not commonly decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen and prevents violent bumping.

Determination of Nitrogen in the presence of Nitrates.

THE KJELDAHL-GUNNING-JODLBAUER PROCESS: The requisite quantity of substance to be analyzed (usually 0·5 to 5 gm.) is put into a digestion flask and 30 c.c. of sulphuric acid containing 2 gm. of salicylic acid are then *quickly* poured over the substance so as to cover it at once. To do this the two acids should be mixed together in a beaker and the latter emptied into the flask. The latter is allowed to stand for 10 minutes, generally in the cold, with occasional shaking. 2 gm. of zinc dust are then added, also a drop of mercury, and the whole gently heated till frothing is over. Potassium sulphate (10 grams) is then added and the process finished as described above.

(In the official Methods of Analysis issued by the Board of Agriculture and Fisheries on Nov. 9, 1908,† the method given is practically as above, with the exception that only 1 gram of salicylic acid is used and 5 grams of sodium thiosulphate are used in place of the 2 gm. of zinc dust. Copper sulphate is mentioned as an alternative to mercury.)

A *blank* determination should be made with all the materials used in either of the above methods. In the case of the Kjeldahl-Gunning process 1 gram of pure cane-sugar should be heated with 20 c.c. of sulphuric acid, mercury and potassium sulphate being added, etc., and the distillate received into 5 c.c. of $^{N}/_{5}$ acid. To this 5 c.c. of $^{N}/_{5}$ soda are then added, with a drop of methyl orange, and $^{N}/_{5}$ acid run in until a pink colour appears. With good acid 20 c.c. give "blanks" ranging between 0·2 and 0·6 c.c. $^{N}/_{5}$ acid. This amount is of course deducted from the amounts of acid neutralized in actual determinations. The use of the cane-sugar is to reduce any trace of nitrates that may be present in the sulphuric acid.

NOTE.—Some substances froth considerably during the distillation with soda into standard acid. This may generally be prevented by adding a small piece of solid paraffin, when the distillation proceeds quietly as usual. In the case of cheese, milk, etc. Brown‡ recommends that the solution obtained after decomposition by sulphuric acid be diluted with water to about 100 c.c. and boiled briskly in the digestion flask until only about 40 c.c. remain. On transferring to the distillation flask, diluting, and adding NaOH etc. as usual, the distillation, can be carried out without the least trouble.

7. Method of Ronchèse.||

This method depends on the fact that in the presence of a large excess of formaldehyde ammonium salts form hexamethylene-

* Some operators prefer to close the distilling flask with a caoutchouc stopper, through which in addition to the distilling tube, a funnel with tap is fixed for running in the alkali. This is to guard against possible loss of ammonia.

† Board of Agriculture and Fisheries. Statutory Rules and Orders, 1908. No. 964.

‡ *C. N.* 1910, **102**, 51. || *J. Pharm. Chem.* 1907, 611, and *Analyst*, **32**, 303.

tetramine, $N_4(CH_2)_6$ (see under Formaldehyde). The liberated acid titrated directly with standard alkali gives a measure of the combined ammonia. The method is interesting, and obviates distillation, but is of limited scope. J. M. Wilkie* has improved it, and H. G. Bennett† has applied it to the determination of hide-substance in leather and tannery liquors.

ACIDIMETRY OR THE TITRATION OF ACIDS.

THIS operation is simply the reverse of all that has been said of alkalies, and depends upon the same principles as have been explained in alkalimetry.

With liquid acids, such as hydrochloric, sulphuric, or nitric, the strength is generally taken by means of the hydrometer or specific-gravity bottle, and the amount of real acid in the sample ascertained by reference to the tables constructed by Lunge and his pupils.

In the case of titrating concentrated acids of any kind it is preferable in all cases to weigh accurately a small quantity, dilute to a definite volume, and take an aliquot portion for titration.

Delicate End-reaction in Acidimetry.

If an alkali iodate or bromate be added to a solution of an alkali iodide in the presence of a mineral acid, iodine is set free and remains dissolved in the excess of alkali iodide, giving the solution the well-known colour of iodine. This reaction has long been known, and is capable of being used with excellent effect as an indicator for the delicate titration of acids, and therefore of alkalies, by the residual method. Kjeldahl, for instance, uses it in his ammonia process, where the distillate contains necessarily an excess of standard acid. The reaction is definite in character, and may be used in various ways in volumetric processes. For instance, potassium bromate liberates iodine in exact proportion to its contained oxygen in the presence of excess of dilute mineral acid, and the iodine so liberated may be accurately titrated with sodium thiosulphate. In acidimetry, however, the method is simply used for its exceeding delicacy as an end-reaction, one drop of $^{N}/_{100}$ sulphuric, nitric, or hydrochloric acid being quite sufficient to cause a deep blue colour in the presence of starch.

The adjustment of the standard liquids is made as follows:— 2 or 3 c.c. of $^{N}/_{10}$ acid are run into a flask, diluted somewhat with water, and a crystal or two of potassium iodide thrown in. 1 or 2 c.c. of a 5 per cent. solution of potassium iodate are then added, which at once produces a brown colour, due to the liberation of iodine. A solution of sodium thiosulphate is added

* *J. S. C. I.* 1910, **29**, 6. † *J. S. C. I.* 1909, **28**, 291.

from a burette, with constant shaking, until the colour is nearly discharged ; a few drops of clear freshly prepared starch solution are now poured in, and the blue colour removed by the very cautious addition of thiosulphate. The quantity of thiosulphate used represents the comparative strengths of it and of the standard acid, and is used as the basis of calculation in other titrations. The first discharge of the blue colour must be taken in all cases as the correct ending, because on standing a few minutes the blue colour returns, due to some obscure reaction from the thiosulphate. This has been probably regarded as one of the drawbacks of the process, and another is the instability of the thiosulphate solution ; but these by no means invalidate its accuracy, moreover, it possesses the advantage of being applicable to excessively dilute solutions, and may be used by artificial light. The organic acids cannot be determined by this method, the action not being regular. Neutral alkali and alkaline earthy salts do not interfere, but salts of the organic acids and borates must be absent.

ACETIC ACID.

$C_2H_4O_2 = 60{\cdot}03.$

In consequence of the discrepancies existing between the sp. gr. of strong acetic acid and its actual strength, the hydrometer readings are not reliable ; but the volumetric determination is now rendered extremely accurate by using phenolphthalein as indicator, acetates of the alkalies and alkaline earths having a perfectly neutral behaviour to this indicator. Even coloured vinegars may be titrated when highly diluted. Where, however, the colour is too dark for this method to succeed, Pettenkofer's method of procedure is the best, and this is endorsed by A. R. Leeds.* The latter takes 50 c.c. of the vinegar and 50 c.c. of water with a drop of phenolphthalein, then adds $^{N}/_{10}$ baryta to slight excess. This causes the organic colouring matters to separate either in the cold or on warming, and the excess of baryta is then found by titration with $^{N}/_{10}$ acid and turmeric paper.

Several processes have at various times been suggested for the accurate and ready determination of acetic acid, among which is that of Greville Williams, by means of a standard solution of lime syrup. The results obtained were very satisfactory.

C. Mohr's process consists in adding to the acid a known excessive quantity of precipitated neutral and somewhat moist calcium carbonate. When the decomposition is as nearly as possible complete in the cold, the mixture must be heated to expel the CO_2 and to complete the saturation ; the residual carbonate is then brought upon a filter, washed with boiling water, treated with excess of normal acid and titrated back with alkali.

* *J. Am. C. S.* **17**, 741.

In testing the impure brown pyroligneous acid of commerce, this method has given fairly accurate results.*

The titration of acetic acid or vinegar may also be performed by the ammonio-cupric solution described on p. 56.

1. **Free Mineral Acids in Vinegar.**—Hehner has devised an excellent method for this purpose.†

Acetates of the alkalies are always present in commercial vinegar; and when such vinegar is evaporated to dryness, and the ash ignited, the alkalies are converted into carbonates having a distinctive alkaline reaction on litmus; if, however, the ash has a neutral or acid reaction, some free mineral acid must have been present. The alkalinity of the ash is diminished in exact proportion to the amount of mineral acid added to the vinegar as an adulterant.

METHOD OF PROCEDURE: 50 c.c. of the vinegar are mixed with 25 c.c. of $^N/_{10}$ soda or potash, evaporated to dryness, and ignited at a low red heat to convert the acetates into carbonates; when cooled, 25 c.c. of $^N/_{10}$ acid are added; the mixture heated to expel CO_2, and filtered; after washing the residue, the filtrate and washings are exactly titrated with $^N/_{10}$ alkali; the volume so used equals the amount of mineral acid present in the 50 c.c. of vinegar.

1 c.c. $^N/_{10}$ alkali = 0·0049 gm. H_2SO_4 or 0·003647 gm. HCl.

If the vinegar contains more than 0·2 per cent. of mineral acid, more than 25 c.c. of $^N/_{10}$ alkali must be used to the 50 c.c. vinegar before evaporating and igniting.

2. **Acetates of the Alkalies and Earths.**—These salts are converted by ignition into carbonates, and can be then residually titrated with normal acid; no other organic acids must be present, nor must nitrates, or similar compounds decomposable by heat. 1 c.c. normal acid = 0·06 gm. acetic acid.

3. **Metallic Acetates.**—Neutral solutions of lead and iron acetates may be precipitated by an excess of normal sodium or potassium carbonate, the precipitate well boiled, filtered, and washed with hot water, the filtrate and washings made up to a definite volume, and an aliquot portion titrated with $^N/_{10}$ acid; the difference between the quantity so used and calculated for the original volume of alkali will represent the acetic acid.

If such solutions contain free acetic or mineral acids, they must be exactly neutralized previous to treatment.

If salts other than acetates are present, the process must be modified as follows:—

METHOD OF PROCEDURE: Precipitate with alkali carbonate in excess, exactly neutralize with hydrochloric acid, evaporate the whole or part to dryness, ignite to convert the acetates into carbonates, then titrate residually with normal acid. Any organic acid other than acetic will, of course, record itself in terms of acetic acid.

* A. R. Leeds (*loc. cit.*) has not found this method to answer, which I think must be due to using dried calcium carbonate. I have only used it for commercial wood acid, and the figures obtained by me were the highest among several other methods; but it is important to mention that the $CaCO_3$ should not be thoroughly dried, and that its alkalinity should be known.

† *Analyst* **1**, 105.

4. Commercial Acetate of Lime.—The methods just described are often valueless in the case of this substance, owing to the presence of tarry matters, which readily produce an excess of carbonates.

Fresenius* adopts the following process for tolerably pure samples :

METHOD OF PROCEDURE : 5 gm. are weighed and transferred to a 250 c.c. flask, dissolved in about 150 c.c. of water, and 70 c.c. of normal oxalic acid added ; the flask is then well shaken, and filled to the mark, 2 c.c. of water are added to allow for the volume occupied by the precipitate, the whole is again well shaken and left to settle. The solution is then filtered through a dry filter into a dry flask ; the volume so filtered must exceed 200 c.c.

100 c.c. are first titrated with normal alkali and litmus ; or, if highly coloured, by help of litmus or turmeric paper; the volume used multiplied by 2·5 will give the volume for 5 gm.

Another 100 c.c. are precipitated with solution of pure calcium acetate in slight excess, warmed gently, the precipitate allowed to settle somewhat, then filtered, well washed, dried, and strongly ignited, in order to convert the oxalate into calcium carbonate or oxide, or a mixture of both. The residue so obtained is then decomposed with excess of normal acid, and titrated residually with normal alkali. By deducting the volume of acid used to neutralize the precipitate from that of the alkali used in the first 100 c.c., and multiplying by 2·5, there is obtained the volume of alkali expressing the weight of acetic acid in the 5 gm. of acetate.

In the case of very impure and highly coloured samples of acetate, it is only possible to determine the acetic acid by repeated distillations with phosphoric acid and water to incipient dryness, and then titrating the acid direct with $/_{10}$ alkali, each c c. of which represents 0·006 gm. acetic acid.

The distillation is best arranged as suggested by Stillwell and Gladding, or later by Harcourt Phillips.†

METHOD OF PROCEDURE : A 100 to 120 c.c. retort, the tubulure of which carries a small funnel fitted in with a rubber stopper, and the neck of the funnel stopped tightly with a glass rod shod with elastic tube, is supported upon a stand in such a way that its neck inclines upwards at about forty-five degrees : the end of the neck is drawn out, and bent so as to fit into the condenser by help of an elastic tube. The greater part of the retort neck is coated with flannel, so as to prevent too much condensation.

1 gm. of the sample being placed in the retort, 10 c.c. of a 40 per-cent. solution of P_2O_5 are added, together with as much water as will make about 50 c.c. A small naked flame is used, and if carefully manipulated the distillation may be carried on nearly to dryness without endangering the retort. After the first operation the retort is allowed to cool somewhat, then 50 c.c. of hot water added through the funnel, another distillation made as before, and the same repeated a third time, which will suffice to carry over all the acetic acid. The distillate is then titrated with alkali and phenolphthalein.

By this arrangement the frothing and spirting is of no consequence, and the whole process can be completed in less than an hour. The results are excellent for technical purposes.

Weber‡ has devised a ready and fairly accurate method of determining the real acetic acid in samples of acetate of lime, based on the fact that acetate of silver is insoluble in alcohol.

* *Z. a. C.* **13**, 153. † *C. N.* **53**, 181. ‡ *Z. a. C.* **24**, 614.

METHOD OF PROCEDURE: 10 gm. of the sample in powder are placed in a 250 c.c. flask, a little water added, and heated till all soluble matters are extracted, cooled, and made up to the mark; 25 c.c. are then filtered through a dry filter, put into a beaker, 50 c.c. of absolute alcohol added, and the acetic acid at once precipitated with an alcoholic solution of silver nitrate. The silver acetate, together with any chloride, sulphate, etc., separates free from colour. The precipitate is brought on a filter, well washed with 60 per-cent. alcohol till the free silver is removed; precipitate is then dissolved in weak nitric acid, and titrated with $^N/_{10}$ salt solution. Each c.c. represents 0·006 gm. acetic acid.

Several trials made in comparison with the distillation method with phosphoric acid gave practically the same results.

A good technical method has been devised by Grimshaw.*

METHOD OF PROCEDURE: 10 gm. of the sample are treated with water and an excess of sodium bisulphate ($NaHSO_4$), the mixture diluted to a definite volume, filtered, and a measured portion of the filtrate titrated with standard alkali; a similar portion meanwhile is evaporated to dryness, with repeated moistening with water to drive off all free acetic acid. The residue is dissolved and titrated with standard alkali, when the difference between the volume now required and that used in the original solution will correspond to the acetic acid in the sample. Litmus paper is the proper indicator.

BORIC ACID AND BORATES.

Boric anhydride $B_2O_3 = 70$.

THE soda in borax may, according to Thomson, be very accurately determined by titrating the salt with standard H_2SO_4 and methyl orange or lacmoid paper. Litmus and phenacetolin give very doubtful end-reactions: phenolphthalein is utterly useless.

EXAMPLE: 1·683 gm. sodium pyroborate in 50 c.c. of water required in one case 16·7 c.c. normal acid, and in a second 16·65 c.c. The mean of the two represents 0·517 gm. Na_2O. Theory requires 0·516 gm.

The determination of boric acid, as such, formerly presented great difficulties, and no volumetric method of any value was available. R. T. Thomson† has removed this difficulty by finding a method easy of execution and of fair accuracy.

METHOD OF PROCEDURE: To determine boric acid in articles of commerce it is necessary to use methyl orange, to which indicator boric acid is perfectly neutral. In the case of boric acid in borax 1 gm. is dissolved in water, methyl orange added, and then dilute sulphuric acid till the pink colour just appears. Boil for a short time to expel CO_2, cool, and add normal or fifth-normal soda till the pink colour of the methyl orange (a little more of which should be added if necessary) just assumes a pure yellow tinge. At this stage all the boric acid will exist in the free state. Add glycerin in such proportion that the total solution after titration will contain 30 per cent. at least, then add a little phenolphthalein, and lastly normal or fifth-normal soda (free from CO_2) from a burette until a permanent pink colour is produced. More glycerin may be added during the determination if it is found necessary. The proportion of boric acid present is calculated from the number of c.c. of soda consumed.

* Allen's *Organic Analysis*, **1**, 3rd edition, 479.

† *J. S. C. I.* **12**, 432.

1 c.c. normal NaOH $=0{\cdot}0620$ gm. H_3BO_3
1 c.c. ,, ,, $=0{\cdot}0505$ gm. $Na_2B_4O_7$
1 c.c. ,, ,, $=0{\cdot}0955$ gm. $Na_2B_4O_7+10H_2O$

In the case of boric acid of commerce, which generally contains salts of ammonium, 1 gm. may be dissolved in hot water, a slight excess of sodium carbonate added, and the solution boiled down to about half its bulk to expel ammonia. Any precipitate which appears may then be filtered off, and the filtrate titrated as already described.

The method may also be applied to boracite and borate of lime by dissolving 1 gm. of either of these minerals in dilute hydrochloric acid with the aid of heat, nearly neutralizing with caustic soda, boiling to expel CO_2, cooling, exactly neutralizing to methyl orange, and continuing the determination as in borax. If much iron is present, however, it should be removed by a preliminary treatment with sodium carbonate and removal of oxide of iron as well as the carbonates of calcium and magnesium by filtration.

L. C. Jones* has based a method of titrating boric acid upon the fact that when a solution of the acid is mixed with one of mannitol, a much stronger acidic character is developed from the boric acid than it naturally possesses (a similar effect occurs with glycerin), and further, that boric acid alone in solution in moderate amount has not the slightest action on a solution containing potassium iodide and iodate. Therefore, if a given solution containing boric acid be mixed with iodide and iodate, the acid set free by addition of a mineral acid, and the free iodine so produced exactly destroyed by thiosulphate, there results a colourless liquid containing the boric acid in a free state and ready to be titrated by any convenient method.

Method of Procedure: The solution, about 50 c.c., containing the boric compound and about 0·1 gm. of boric acid, is acidified distinctly with hydrochloric acid, but any large excess must be removed with soda. 5 c.c. of a 10 per-cent, solution of barium chloride are then added. In a separate beaker the iodide and iodate mixture, say 10 c.c. of a 25 per-cent. solution of iodide and the same volume of a saturated solution of iodate, together with starch indicator is placed—the quantity must be sufficient to liberate an amount of iodine equivalent at least to the free HCl in the boric solution; the colour of the starch iodide which is usually liberated from this mixture is removed by a dilute solution of sodium thiosulphate. To this neutral solution of iodide and iodate a single drop of the boric solution is added by a glass rod; if a blue colour appears it is evident that the boric solution is acid with free HCl and the boric acid is in a free condition. The solutions are then mixed and the free iodine removed by cautious addition of thiosulphate. The mixture is then colourless and contains only starch, neutral chloride, potassium tetrathionate, iodide and iodate, with all the B_2O_3 in a free state. Any CO_2 will have been removed by the barium chloride.

The titration is now begun by adding a few drops of phenolphthalein and $^{N}/_{5}$ caustic soda run in from the burette until a strong red colour is shown; a pinch of mannitol is then thrown in which bleaches the colour, more soda and more mannitol are in turn added until the colour is permanent. As a rule 1 or 2 gm. of mannitol suffice for a determination. The amount of B_2O_3 is calculated on the assumption that under the above mentioned conditions 1 mol. of the acid requires 2 mol. of sodium hydroxide. Test analyses on calcium borate and colemanite gave satisfactory results and within a very short time. Silicates and fluorides do not interfere, but ammonium salts must be removed by boiling with alkali previous to adopting the process, owing to their well known effect on the indicator.

* *Am. J. S.*, 1898, 147–153.

Schwartz* recommends the glycerin method in the case of boracite to be carried out as follows :—

1 or 2 gm. of the finely powdered material are mixed with 5 to 10 c.c. of strong hydrochloric acid, made up to about 50 or 100 c.c. with water, and digested with stirring for several hours at ordinary temperature. The process may be hastened by heating, but in that case a reflux condenser may be necessary to avoid loss of boric acid. In either case the liquid is filtered, residue washed, and the filtrate rendered exactly neutral to methyl orange with $^{N}/_{5}$ soda (free from CO_2). The volume is made up to 100 or 200 c.c., then 25 or 50 c.c. mixed with the same volume of absolutely neutral glycerin, diluted somewhat, then titrated with phenolphthalein and $^{N}/_{5}$ soda.

Boric Acid in Milk, Butter, and other Foods.—R. T. Thomson†. 1 to 2 gm. of sodium hydrate are added to 100 c.c. of milk, and the whole evaporated to dryness in a platinum dish. The residue is cautiously but thoroughly charred, heated with 20 c.c. of water, and hydrochloric acid added drop by drop until all but the carbon is dissolved. The whole is transferred to a 100 c.c. flask, the bulk not being allowed to exceed 50 or 60 c.c., and 0·5 gm. dry calcium chloride added. To this mixture a few drops of phenolphthalein are added, then a 10 per-cent. solution of caustic soda, till a permanent slight pink colour is perceptible, and finally 25 c.c. of lime-water. In this way all the P_2O_5 is precipitated as calcium phosphate. The liquid is made up to 100 c.c. thoroughly mixed and filtered through a dry filter. To 50 c.c. of the filtrate (equal to 50 c.c. of the milk) normal sulphuric acid is added till the pink colour is gone, then methyl orange, and the addition of the acid continued until the yellow is just changed to pink. $^{N}/_{5}$ caustic soda is now added till the liquid assumes the yellow tinge, excess of soda being avoided. At this stage all acids likely to be present exist as salts neutral to phenolphthalein, except boric acid (which, being neutral to methyl orange, exists in the free condition), and a little CO_2, which it is absolutely necessary to expel by boiling for a few minutes. The solution is cooled, a little phenolphthalein added, and as much glycerin as will give at least 30 per cent. of that substance in the solution, then titrated with $^{N}/_{5}$ caustic soda till a distinct permanent pink colour is produced. Each c.c. of the soda is equal to 0·0124 gm. crystallized boric acid. A series of experiments with this process showed that no boric acid was precipitated with the phosphate of lime so long as the solution operated upon did not contain more than 0·2 per cent. of crystallized boric acid, but when stronger solutions were tested, irregular results were obtained. The charring of the milk is apt to drive off boric acid, but by carefully carrying the incineration only so far as is necessary to secure a residue which will yield a colourless solution, no appreciable loss occurs.

There is no doubt that CO_2 must be got rid of in titrating boric acid with phenolphthalein, and hence it is necessary to boil the solution. Some operators therefore do this in a flask with upright condenser to avoid the loss of boric acid. It is doubtful, however, whether by this confined escape, the gas is got rid of as easily as is thought. L. de Koningh‡ gives the results of experiments made in this manner, and shows that a dilute solution of the acid may be boiled even up to fifteen minutes in an open vessel (which is longer than necessary), with the loss of a very faint trace of the acid. The same operator also advocates the removal of phosphoric acid, which is nearly always present in foods, by adding a slight excess of sodium carbonate to the boric acid liquid, then cautiously adding calcium chloride ; this precipitates any phosphate and the excess of carbonate, while the borate in very dilute solution is not affected. On now adding a solution of ammonium carbonate containing an excess of free ammonia the excess of lime is precipitated. By boiling the clear solution with excess of sodium carbonate the ammonium compounds are quickly expelled, and the titration may be carried on as before described.

A new process is also described in the same article by which the boric acid may

* *Chem. Zeit.*, 1899, 497. † *Glasgow City Anal. Soc. Repts.*, 1895, p. 3.

‡ *J. Am. C. S.* 1897, 385.

be determined after the removal of the P_2O_5 by means of magnesium mixture ; the filtrate is mixed with excess of sodium carbonate and heated, the precipitate of magnesia is removed by filtration, the filtrate evaporated to dryness to render the rest of the magnesia insoluble, and the residue is then treated with a little water and filtered. The boric acid may then be titrated according to Thomson's glycerin method. As a test experiment, 0·1 gm. of boric acid was dissolved in aqueous soda, then mixed with 100 gm. of oatmeal and incinerated ; from the ash, 0·095 gm. of boric acid was recovered.

A rapid method for determining boric acid in *BUTTER* has been worked out by H. Droop Richmond and J. B. P. Harrison.* 25 gm. of the butter are weighed out into a beaker, and 25 c.c. of a solution containing 6 gm. of milk sugar and 4 c.c. of normal sulphuric acid in 100 c.c. are added. The beaker is placed in the water oven until the fat has just melted and the mixture is well stirred. After allowing the aqueous portion to settle for a few minutes 20 c.c. are pipetted out, a little phenolphthalein added, brought to the boiling point, and titrated with semi-normal caustic soda until a faint pink colour just appears. 12 c.c. of neutral glycerin are now added, and the further titration carried on till a pink colour appears. The difference between the two titrations multiplied by 0·0368 gives the amount of boric acid in 20 c.c., and this multiplied by

$$\frac{100 + \text{percentage of water in the butter}}{20}$$

will give the percentage of boric acid. The determination is not affected by the phosphoric or butyric acid, or milk sugar present in the butter.

For the determination of boric acid in meat C. Fresenius and G. Popp† adopt the following method with good results :—

10 gm. of the chopped meat is triturated in a mortar with 40 to 80 gm. of anhydrous sodium sulphate, and dried in the water oven ; the mass is then finely powdered, if necessary with the addition of more sodium sulphate, introduced into a 300-c.c. Erlenmeyer flask, and 100 c.c. of methylic alcohol added. After standing for twelve hours, the alcohol is distilled off ; 50 c.c. more methylic alcohol are poured on to the residue, and this is again distilled off. The distillate is finally made up with methylic alcohol to 150 c.c., and 50 c.c. of this are mixed with 50 c.c. of water and 50 c.c. of 50 per-cent, glycerin solution containing phenolphthalein, and carefully neutralized with soda ; after thoroughly mixing the liquid, it is titrated with $N/20$ soda, 1 c.c. of soda = 0·0031 gm. of crystallized boric acid.

CARBONIC ACID AND CARBONATES.

All carbonates are decomposed by strong acids ; the carbonic acid which is liberated splits up into water and carbonic anhydride (CO_2), which latter escapes in the gaseous form.

It will readily be seen, from what has been said previously as to the determination of the alkaline earths, that carbonic acid in combination can be determined volumetrically with a very high degree of accuracy (see p. 72).

The carbonic acid to be determined may be brought into combination with either calcium or barium, these bases admitting of the firmest combination as neutral carbonates.

If the carbonic acid exist in a soluble form as an alkali mono-

* *Analyst* **27**, 179. † *Chem. Centr.*, 1897, **2**, 69.

carbonate, the decomposition is effected by the addition of barium or calcium chloride as before directed; if as bicarbonate, or a compound between the two, ammonia must be added with either of the chlorides.

As solution of ammonia frequently contains traces of CO_2, this must be removed by the aid of barium or calcium chloride previous to use.

1. Carbonates Soluble in Water.

It is necessary to remember that when calcium chloride is used as the precipitant in the cold amorphous calcium carbonate is first formed; and as this compound is sensibly soluble in water, it is necessary to convert it into the crystalline form. In the absence of free ammonia this can be accomplished by boiling. When ammonia is present, the same end is obtained by allowing the mixture to stand for eight or ten hours in the cold, or by heating for an hour or two to 70-80° C. With barium the precipitation is regular.

Another fact is that when ammonia is present, and the precipitation occurs at ordinary temperatures, ammonium carbamate is formed and the barium or calcium carbonate is only partially precipitated. This difficulty is overcome by heating the mixture nearly to boiling for a couple of hours, and is best done by passing the neck of the flask through a retort ring, and immersing the flask in boiling water.

When caustic alkali is present in the substance to be examined, it is advisable to use barium as the precipitant; otherwise, for all volumetric determinations of CO_2 calcium is to be preferred, because the precipitate is much more quickly and perfectly washed than the barium compound.

EXAMPLE: 1 gm. of pure anhydrous sodium carbonate was dissolved in water, precipitated while hot with barium chloride, the precipitate allowed to settle well, the clear liquid decanted through a moist filter, more hot water containing a few drops of ammonia poured over the precipitate, this treatment being repeated so that the bulk of the precipitate remained in the flask, being washed by decantation through the filter; when the washings showed no trace of chlorine, the filter was transferred to the flask containing the bulk of the precipitate, and 20 c.c. of normal nitric acid added, then titrated back with normal alkali, of which 1·2 c.c. was required = 18·8 c.c. of acid; this multiplied by 0·022, the coefficient for carbonic acid, gave 0·4136 gm. CO_2 = 41·36 per cent., or multiplied by 0·053, the coefficient for sodium carbonate, gave 0·9964 gm. instead of 1 gm.

2. Carbonates Soluble in Acids.

It sometimes occurs that substances have to be examined for carbonic acid which do not admit of being treated as above described, such, for instance, as white lead, calamine, carbonates of magnesia, iron, and copper, cements, mortar, and many other substances. In these cases the carbonic acid must be evolved from the combination

by means of a stronger acid, and conducted into an absorption apparatus containing ammonia, then precipitated with calcium chloride, and titrated as before described.

The following form of apparatus (fig. 33) affords satisfactory results.

Fig. 33

Method of Procedure: The weighed substance from which the carbonic acid is to be evolved is placed in *b* with a little water; the tube *d* contains strong hydrochloric acid, and *c* broken glass wetted with ammonia free from carbonic acid. The flask *a* is about one-eighth filled with the same ammonia; the bent tube must not enter the liquid. When all is ready and the rubber stoppers tight, warm the flask *a* gently so as to fill it with vapour of ammonia, then open the clip and allow the acid to flow gradually upon the material, which may be heated until all carbonic acid is apparently driven off; then by boiling and shaking the last traces can be evolved, and the operation ended. When cool, the apparatus may be opened, the end of the bent tube washed into *a*, and also a good quantity of boiled distilled water passed through *c*, so as to carry down any ammonium carbonate that may have formed. Then add solution of calcium chloride, boil, filter, and titrate the precipitate as before described.

During the filtration, and while ammonia is present, there is a great avidity for carbonic acid, therefore boiling water should be used for washing, and the funnel kept covered with a small glass plate.

In many instances CO_2 may be determined by its equivalent in chlorine with $^N/_{10}$ silver and chromate, as on page 143.

3. Carbonic Acid Gas in Waters, etc.

The carbonic acid existing in waters as neutral carbonates of the alkalies or alkaline earths may very elegantly and readily be titrated directly by $^{N}/_{10}$ acid (see p. 73).

Well or spring water, and also mineral waters, containing free carbonic acid gas, can be examined by collecting measured quantities of them at their source, in bottles containing a mixture of calcium and ammonium chlorides, afterwards heating the mixture in boiling water for one or two hours, and titrating the precipitate as before described.

Pettenkofer's method with caustic baryta or lime is in general use. Lime water may be used instead of baryta with equally good results, but care must be taken that the precipitate is crystalline.

The principle of the method is that of removing all the carbonic acid from a solution, or from a water, by excess of baryta or lime water of a known strength ; and, after absorption, finding the excess of baryta or lime by titration with $^{N}/_{10}$ acid and turmeric paper.

The following course is the best to be pursued in this method for ordinary drinking waters not containing large quantities of carbonic acid :—

METHOD OF PROCEDURE : 100 c.c. of the water are put into a flask with 3 c.c. of strong solution of calcium or barium chloride, and 2 c.c. of saturated solution of ammonium chloride ; 45 c.c. of baryta or lime water, the strength of which has been previously ascertained by means of decinormal acid, are then added, the flask well corked and put aside to settle ; when the precipitate has fully subsided, take out 50 c.c. of the clear liquid with a pipette, and titrate it with decinormal acid. The quantity required must be multiplied by 3, there being 50 c.c. only taken ; the number of c.c. so found must be deducted from the original quantity required for the baryta or lime solution added ; the remainder multiplied by 0·0022 will give the weight of carbonic acid existing free and as bicarbonate in the 100 c.c.

The addition of the barium or calcium chloride and ammonium chloride is made to prevent any irregularity which might arise from alkaline carbonates or sulphates, or from magnesia.

A more accurate method of determining CO_2 in its various states of existence in drinking waters has been used for some years past. It is described by C. A. Seyler.*

Whatever may really be the condition under which CO_2 exists in natural waters, and there is difference of opinion on the point, it is sufficient for all practical purposes to assume that it occurs in three forms, namely : first, as monocarbonates of alkalies or alkaline earths ; second, as bicarbonates of the same ; and third, as free CO_2. Seyler proposes to distinguish the first as fixed and the two others as volatile CO_2, inasmuch as the gas existing as bicarbonate may be almost, and the free gas completely, dispelled by boiling. On the assumption that the half-bound acid (*i.e.*, as bicarbonate) is equal to the combined, the free CO_2

* *C. N.*, 1894 ; *Analyst*, 1897, p. 312.

may be determined by subtracting the combined from the volatile as found by Pettenkofer's process—this, however, is inaccurate with small quantities and tedious. What is required is a method of determining the free CO_2 independently.

Pettenkofer's method has been modified by Trillich, Lunge, and Seyler, and the modifications have been carefully investigated by Ellms and Beneker,* who have come to the conclusion that Seyler's method is the most accurate.

The essential details of the process are as follows :—

The free carbonic acid is determined by placing 100 c.c. of the sample in a glass cylinder with 25 to 30 drops of a neutral solution of phenolphthalein. To the sample is then added $^{N}/_{20}$ sodium carbonate, stirring carefully and thoroughly until a faint permanent pink colour is obtained.

METHOD OF PROCEDURE: 1. The titration can conveniently be performed in a Nessler cylinder, approximately 18 cm. long by 3 cm. in diameter, graduated for 50 and 100 c.c. The stirring rod is bent at its lower end into the form of a circle, and then turned so as to stand at right-angles to the rod. A comparison cylinder containing the same amount of water as the titrating cylinder is found to aid in the determination of the end-point.

2. The larger part of the sodium carbonate solution should be added quickly, and the strong pink colour formed should be discharged by stirring and mixing with the rod. The titration can then be cautiously completed, until colour remains permanent. The sodium carbonate solution should be prepared with freshly ignited sodium carbonate, and with air-free water. The exposure of this solution to the air should be avoided as much as possible, as sodium bicarbonate is readily formed, which renders it useless for this titration where accurate results are desired.

3. With waters that are high in free and half-bound carbonic acid it is better to use less than 100 c.c. for the titration. With such a water, care is necessary in transferring the sample to the cylinder in order to avoid loss of CO_2. Too vigorous stirring of the water is also to be avoided for the same reason.

The fixed carbonic acid, from which the half-bound acid is estimated, is determined according to the method of Hehner (p. 74). Seyler uses methyl orange as the indicator for this titration, but lacmoid is preferable.

In the absence of free CO_2 in a water, the half-bound may equal the fixed, in which case it would be neutral to phenolphthalein. If, however, the water is alkaline to phenolphthalein, the half-bound CO_2 does not equal the fixed; or, in other words, a portion of the carbonates of the bases exist in solution without the assistance of any half-bound CO_2. In such a case the half-bound acid is obtained by first determining the fixed CO_2 by means of lacmoid. From this is deducted an amount of CO_2 equal to twice the quantity indicated by the acid required to discharge the pink colour produced by phenolphthalein. The difference is the amount of half-bound CO_2 which is present. These titrations may be made on the same sample, in which case the "phenolphthalein alkalinity" is first determined and then followed by the titration with lacmoid; or they may be made on separate samples.

The principles upon which the above procedure is based have been pointed out above.

These titrations involve no especial difficulties, and can be easily and quickly carried out. $^{N}/_{20}$ solutions of sulphuric acid and sodium carbonate were used by the experimenters. Seyler has prepared a series of formulæ for calculating the results, which simplifies the work somewhat. If results are obtained with 100 c.c. of the sample and the reagents employed are $^{N}/_{20}$, the following formulæ express the results in parts per million :—

I. For waters acid or neutral to phenolphthalein :—

* *J. Am. C. S.* **23**, 405.

Free carbonic acid	$=4{\cdot}4\ p$
Fixed or half-bound carbonic acid	$=4{\cdot}4\ m$
Volatile carbonic acid	$=4{\cdot}4\ (m+p)$
Total carbonic acid	$=4{\cdot}4\ (2m+p)$

p = c.c. $^{N}/_{20}$ sodium carbonate solution required to produce a pink colour with phenolphthalein in 100 c.c. of the water; and

m = c.c. $^{N}/_{20}$ sulphuric acid solution required to obtain the end-point with methyl orange or lacmoid in the same volume of water.

II. For waters alkaline to phenolphthalein:—

Fixed carbonic acid	$=4{\cdot}4\ m$
Half-bound or volatile carbonic acid	$=4{\cdot}4\ (m-2p')$
Total carbonic acid	$=4{\cdot}4\ (2m-p')$

m = c.c. $^{N}/_{20}$ sulphuric acid solution required to obtain end-point with methyl orange or lacmoid in 100 c.c. of the sample.

p' = c.c. $^{N}/_{20}$ sulphuric acid required to discharge the pink colour produced by phenolphthalein in 100 c.c. of the sample.

There is a third case in which free CO_2 might exist in a solution containing free mineral acid, and for which Seyler has given a method with its corresponding formulæ for calculating the results. But such a condition would seldom be found in natural waters.

The errors affecting the accuracy of Seyler's method are those which arise in part from the determination of the free CO_2. The end-point in the titration of the sample with sodium carbonate and phenolphthalein is not entirely satisfactory. The results obtained are usually low, but with care and practice the error from this source should be less than 2 to 3 parts per million, even with considerable amounts of CO_2, and on small amounts it is less still.

The error due to the determination of the fixed carbonic acid, from which the half-bound is derived, arises from those errors involved in the carrying out of Hehner's method, which in good work ought not to exceed 1 to 2 parts per million.

4. Carbonic Acid in Aërated Beverages, etc.

For ascertaining the quantity of CO_2 in bottled aërated waters, such as soda, seltzer, potass, and others, the following apparatus is useful.

Fig. 34 is a brass tube made like a cork-borer, about five inches long, having four small holes, two on each side, and about two inches from its cutting end; the upper end is securely connected with the bent tube from the absorption flask (fig. 35) by means of a vulcanized tube; the flask contains a tolerable quantity of pure ammonia, into which the delivery tube dips; the tube *a* contains broken glass moistened with ammonia.

Everything being ready the brass tube is greased, and the bottle being held in the right hand, the tube is screwed a little aslant through the cork by turning the bottle round, until the holes appear below the cork and the gas escapes into the flask. When all visible action has ceased, after the bottle has been well shaken two or three times to evolve all the gas that can possibly be eliminated, the vessels are quietly disconnected, the tube *a* washed out into the flask, and the contents of the bottle added also; the whole is then precipitated with calcium chloride and boiled, and the precipitate titrated as usual. This gives the total CO_2 free and combined.

To find the quantity of the latter, another bottle of the same manufacture must be evaporated to dryness, and the residue gently ignited, then titrated with normal acid and alkali; the amount of CO_2 in the monocarbonate, deducted from the total, will give the weight of free gas originally present.

The volume may be found as follows:—1000 c.c. of CO_2 at 0°, and 760 mm. weigh 1·9769 gm. (Rayleigh). Suppose, therefore, that the total weight of CO_2 found in a bottle of ordinary soda water was 2·8 gm., and the weight combined with alkali 0·42 gm., this leaves 2·38 gm. CO_2 in a free state—

$$1{\cdot}9769 : 2{\cdot}38 :: 1000 : x = 1204 \text{ c.c.}$$

If the number of c.c. of carbonic acid found is divided by the number of c.c. of soda water contained in the bottle examined, the quotient will be the volume of gas compared with that of the soda water. The volume of the contents of the bottle is ascertained by marking the height of the fluid previous to making the experiment; the bottle is afterwards filled to the same mark with water, emptied into a graduated cylinder and measured; say, the volume was 292 c.c., therefore

$$\frac{1204}{292} = 4{\cdot}12 \text{ vols. } CO_2.$$

Fig. 34.

Fig. 35.

5. Carbonic Acid in Air.

A dry glass globe or bottle capable of being securely closed by a rubber stopper, and holding 4 to 6 litres, is filled with the air to be tested by means of a bellows aspirator; baryta or lime water, containing a little barium chloride, is then introduced in convenient quantity and of known strength as compared with $^N/_{100}$ acid. The vessel is securely closed, and the liquid allowed to flow round the sides at intervals during half an hour or more. When absorption is judged to be complete, the alkaline solution is emptied out quickly into a stoppered bottle, and the excess at once ascertained in a measured portion by $^N/_{100}$ oxalic or hydrochloric acid and turmeric paper as described on p. 55. The final calculation is of course made on the total alkali originally used, and upon the exact measurement of the air-collecting vessel.

It is above all things necessary to prevent the absorption of CO_2 from extraneous sources during the experiment, especially from the

breath of the operator. The error may be reduced to a minimum by carrying on the titration in the vessel itself, which is done by fixing an accurately graduated pipette through the cork or caoutchouc stopper of the air vessel, to the upper end of which is attached a stout piece of elastic tube, closed with a pinch-cock; and this being filled to the 0 mark with dilute standard acid acts as a burette. The baryta or lime solution tinted with phenolphthalein is placed in the air bottle, which must be of colourless glass, and after the absorption of all CO_2 the excess of alkali is found by running in the acid until the colour disappears.*

The cork or stopper must have a second opening to act as ventilator; a small piece of glass tube does very well.

If a freshly made solution of oxalic acid is used containing 2·8636 gm. per litre, each c.c. represents 1 mgm. CO_2. The liquid holds its strength correctly for a day, and can be made as required from a strong solution, say 28·636 per litre.

Another method of calculation is to convert the volume of baryta solution decomposed into its equivalent volume in $^N/_{10}$ acid, 1 c.c. of which $=0·0022$ gm. CO_2 or by measurement at 0° C. and 760 mm. pressure represents 1·119 c.c. The method above described is a combination of those of Pettenkofer and Dalton, and, though much used, is liable to considerable error from various causes.

These errors have been examined by Letts and Blake,† more especially as to absorbing the CO_2 by baryta from a sample of air collected in a glass vessel and titrating with acid, and they show that, in addition to the more obvious sources of error, the action of the alkaline absorbent on the glass is one of importance.

In order to avoid it, they coat both the receiver containing the air sample and the bottle holding the stock of standard solution of baryta with paraffin wax. By this means they at once obtained more concordant results in a series of determinations. They then proceeded to test the degree, both of accuracy and of delicacy, of Pettenkofer's process if carried out with all the available precautions which suggested themselves. For this purpose they employed paraffined receiving vessels, an apparatus for performing the titrations in a vacuum, and burettes of special construction. In addition, an apparatus was used for delivering very accurately measured volumes of pure carbonic anhydride into known volumes of air previously freed from that gas.

Experimenting with such mixtures of the two as occur in air containing about 3 vols. of CO_2 in 10,000, the authors show that with careful work the mean error in the determinations need not exceed $-0·04$ part. The actual quantity of CO_2 added to each

* Some operators prefer a standard mixture of caustic soda or potash containing some barium chloride to the baryta or lime solution. This is adopted by Symons and Stephens with acetic acid as control. The method used by them, which gives excellent results, is explained in their voluminous paper contributed to *J.C.S. Trans.*, 1896, pp. 869-881.

† *Proc. Chem. Soc.* 1896, 192.

receiver full of air, in a series of five experiments, amounted to 0·927 c.c., and the mean amount found to 0·916 c.c., giving, therefore, a mean error of $-0·011$ c.c.

They thus show that Pettenkofer's process, if properly performed, is one of great accuracy and delicacy.

A. H. Gill in a report from the Sanitary and Gas Analysis Laboratory of the Technical Institute at Boston, U.S.A.,* gives a somewhat modified arrangement of the Pettenkofer method. Ordinary green glass bottles of one or two gallons capacity are measured by filling them with water, and the contents in c.c. ascertained, preferably by weighing on a good balance.

The bottles are dried before being used. This may easily be done by rinsing first with alcohol or methylated spirit, draining, then rinsing with ether, and after again draining the bottle is quickly dried by blowing air through it with the ordinary laboratory bellows. If this plan is not used they must be dried, after draining well, in a warm place. A special form of bellows for filling the bottle with air is used by Gill, but the usual aspirator made on the accordion pattern suffices, or a small fan blower, the driving parts of which are connected by rubber bands to render it noiseless, may be used.

The bottle is fitted with a rubber stopper carrying a glass tube, closed by a plug of solid rubber.

The air to be tested is drawn into the bottle by repeated use of the aspirator so as to collect a representative sample, and if the test is made in a room everything should be quiet, and care must be taken to avoid draughts or the proximity of a number of persons.

METHOD OF PROCEDURE: 50 c.c. of the standard barium hydrate are rapidly run into the bottle from a burette (the jet passing entirely through the tube in the stopper), the cap replaced, and the solution spread completely over the sides of the bottle while waiting three minutes for the draining of the burette, before reading, unless it be graduated to deliver 50 c.c. The bottle is now placed upon its side, and shaken at intervals for forty to sixty minutes, taking care that the whole surface of the bottle is moistened with the solution each time. The absorption of the last traces of CO_2 is very slow indeed, half an hour in many cases being insufficient.

At the time at which the barium solution is added the temperature and pressure should be noted. At the end of the above period, shake well to ensure homogeneity of the solution, remove the cap from the tube, and invert the large bottle quickly over a 60 or 70 c.c. glass stoppered bottle, so that the solution shall come in contact with the air as little as possible. Without waiting for the bottle to drain, withdraw a portion of 15 or 25 c.c. with a narrow-stemmed spherical-bulbed pipette and titrate with sulphuric acid † (1 c.c. = 1 mgm. CO_2), using rosolic acid as an indicator. The difference between the number of c.c. of standard acid required to neutralize the amount of barium hydrate (*e.g.*, 50 c.c.) before and after absorption gives the number of milligrams of CO_2 present in the bottle.

* *Analyst* **17**, 184.

† Sulphuric acid, in distinction to oxalic acid, enables one to determine the excess of barium hydrate in presence of the suspended barium carbonate, and also of caustic alkali, which is a frequent impurity of commercial barium hydrate. Professor Johnson, in the American edition of Fresenius' *Quantitative Analysis*, calls attention to the fact that the normal alkali oxalates decompose the alkaline earthy carbonates, so that the reaction continues alkaline if the least trace of soda or potash be present. The sulphuric acid may be prepared by diluting 46·51 c.c. normal sulphuric acid to a litre.

This is expressed in cubic centimetres under standard conditions, and divided by the capacity of the bottle under standard conditions, and the results reported in parts per 10,000. To reduce the air in the bottle to standard conditions, a hygrometric measurement of the air in the room from which the sample was taken is necessary. This in ordinary cases is usually omitted, as the object of the investigation is *comparative* results, as regards the efficiency of ventilation, and the rooms in the same building would not vary appreciably in the amount of moisture in the atmosphere. This correction may make a difference of about 0·15 parts per 10,000.

Another method on the same principle is to attach a bulb apparatus, containing a measured quantity of baryta or lime water, to an aspirator bottle filled with water; the tap of the bottle is opened to such an extent as to allow the air to bubble through the test solution at a moderate rate. The process of titration is the same as above. This method takes longer time, and the volume of air, which should not be less than five or six litres, is ascertained by measuring the volume of water allowed to run out of the aspirator, the rate of flow being regulated so that from two to three hours are required to pass the above volume of air. If a flask, fitted with tubes, is used in place of the bulb apparatus, the titration may be done without transferring the test solution.

6. Scheibler's Calcimeter for the determination of Carbonic Acid by Volume.

This apparatus is adapted for the determination of the CO_2 contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily determining the CO_2 in the bone-black used in sugar refining. The principle upon which the apparatus is founded is simply this :—That the quantity of CO_2 contained in calcium carbonate may be used as a measure of the quantity of that salt itself; and instead of determining, as has usually been the case, the quantity of gas by weight, this apparatus admits of its determination by volume; and it is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish, while, moreover, the operator need possess scarcely any knowledge of chemistry. The results obtained by this apparatus are said to be correct enough for technical purposes.

The apparatus is shown in fig. 36, and consists of the following parts :—

The glass vessel, A, serves for the decomposition of the material to be tested for CO_2, which for that purpose is treated with dilute HCl; this acid is contained, previous to the experiment, in the gutta percha vessel *s*. The glass stopper of A, is perforated, and through it firmly passes a glass tube, to which is fastened the india-rubber tube *r*, by means of which communication is opened with B, a bottle having three openings in its neck. The central opening of this bottle contains a glass tube (*r*) firmly fixed, which is in communication, on the one hand, with A, by means of the flexible india-rubber tube already alluded to, and, on the other hand, *inside* of B, with a very thin india-rubber bladder, K. The neck (*q*) of the vessel B is shut off during the experiment by means of a piece of india-rubber tubing, kept firmly closed with a spring clamp. The only use of this

opening of the bottle B, arranged as described, is to give access of atmospheric air to the interior of the bottle, if required. The other opening is in communication with the measuring apparatus C, a very accurate cylindrical glass tube of 150 c.c. capacity, divided into 0·5 c.c.; the lower portion of this tube C is in communication with the tube D, serving the purpose of controlling the pressure of the gas. The lower part of this tube D ends in a glass tube of smaller diameter, to which

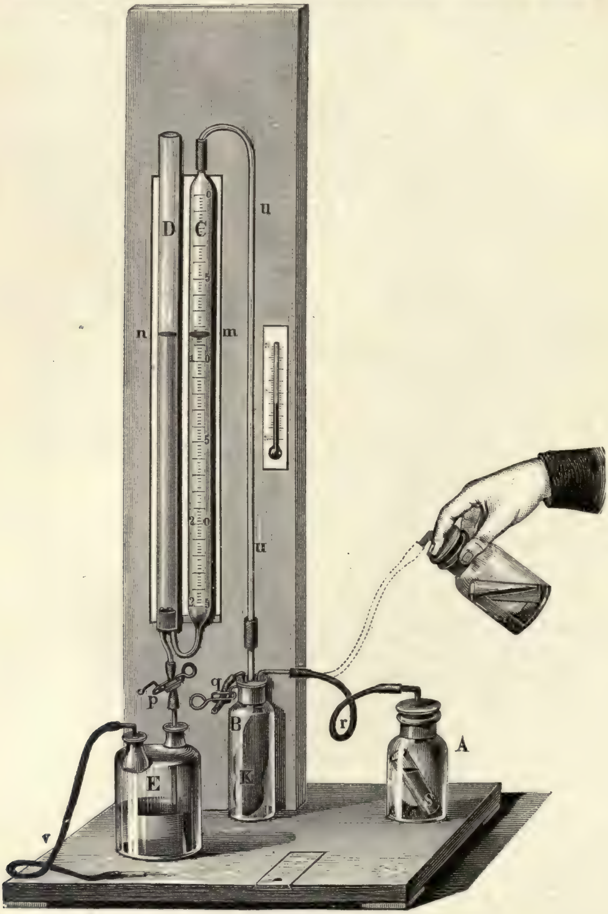


Fig. 36.

is fastened the india-rubber tube *p*, leading to E, but the communication between these parts of the apparatus is closed, as seen at *p*, by means of a spring clamp. E is a water reservoir, and on removal of the clamp at *p*, the water contained in C and D runs off towards E; when it is desired to force the water contained in E into C and D, this can be readily done by blowing with the mouth into V, and opening the clamp at *p*.

Precise directions for the use of this instrument are issued by the makers and need not be repeated here. It has been considerably used for technical purposes, but is liable to serious errors, for which various corrections have to be made, but even then there is room for considerable improvement.

This improvement has been made by A. Marshall,* and the apparatus is shown in fig. 37.

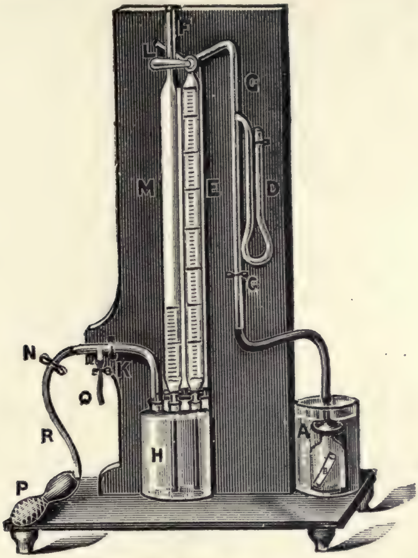


Fig. 37.

It consists of a gas reduction tube M, and a measuring tube E, which both pass through corks to the bottom of the Woulff's bottle H, which is so fitted that the pressure of air in it can be accurately adjusted. It contains some refined petroleum oil of high boiling point, which can be forced into the tubes M and E. M contains such a quantity of air that, if it were reduced to 0° C. and 760 mm. pressure, it would just fill the tube down to a certain mark on it. The tube E is graduated in cubic centimetres, and is fitted at the top with a three-way cock of special design, by means of which it can be brought into communication either with the atmosphere or with the tube G, which leads to the generating vessel A. Branching out of G is the mercury manometer D, which enables one to adjust the pressure inside A, G, and E till it is equal to the atmospheric pressure. The generating vessel A is fitted with a well-ground tubulated stopper, and contains a small glass tube B to hold the acid. It is inserted in the glass water-bath C, which should contain cold water.

Briefly stated, a determination is conducted as follows :—The carbon dioxide is generated by the action of a small volume, 1 c.c., of concentrated hydrochloric acid on a weighed quantity of the substances to be tested ; 0·1 to 0·8 or more gm. should be taken, according to the percentage of carbonic acid it contains. A mixture of air and carbon dioxide passes over into the measuring tube E. When the action is complete, the pressure is adjusted, till the manometer D shows that it is equal to that of the atmosphere. The cock is then turned off, and the pressure is again adjusted till the liquid in M stands at the highest graduation. The volume in E is then read off. This, without any correction whatever, is the volume of carbon dioxide contained in the substance taken. The whole operation does not take more than ten to fifteen minutes.

The gas reduction tube E acts on the same principle as that in Lunge's well-known "gas volumeter." To give absolutely accurate results the level of liquid in M and E should be the same. The density of the petroleum is, however, so

* *J. S. C. I.*, 1898, 1106.

small that the error from this cause never amounts to more than 0·3 c.c. with an apparatus having the dimensions selected by the inventor.

Carbon dioxide is slightly soluble even in heavy petroleum oil, but the solution proceeds very slowly. In the case of this apparatus, if the printed instructions be followed, only a dilute mixture of carbon dioxide can come in contact with the petroleum. The error due to this cause therefore falls well within the limits of experimental error due to other causes.

The error due to the solubility of carbon dioxide in hydrochloric acid is reduced to a minimum by employing a small quantity of concentrated acid; using 1 c.c. of acid of 1·17 sp. gr. it does not amount to more than 0·5 c.c. This error is in the opposite direction to that due to the inequality of the levels in the tubes M and E. Consequently it is to a great extent neutralized by the latter. Concentrated hydrochloric acid dissolves less carbon dioxide than the same volume of dilute acid.

If the generating vessel A be not kept cool a notable quantity of hydrogen chloride is expelled from it, and is slowly reabsorbed as the apparatus cools down again. This, of course, would interfere with the accuracy of the process. During the action the vessel should, therefore, be kept immersed in cold water. The cold-water bath also tends to prevent the temperature of the generating apparatus varying to any perceptible extent. Any error due to the latter cause is, in addition, greatly reduced by the small volume of the generating apparatus, which is not more than 100 c.c.

The following are the chief advantages of the apparatus described:—

1. The quantity of carbon dioxide dissolved in the acid is reduced to a minimum by using a small quantity of concentrated acid.

2. No corrections have to be made for temperature and pressure; consequently no reading of thermometer or barometer need be taken.

3. The total volume of the generating and measuring apparatus being less than 100 c.c., and the generating vessel being immersed in a considerable quantity of cold water, the volume of the air inside it cannot change during a determination to an extent sufficient to introduce a perceptible error.

4. The apparatus is quite simple, and although no barometer or thermometer is required the results are considerably more accurate than those obtained with Scheibler's.

To determine the percentage of $CaCO_3$ in any substance, weigh out accurately 0·224 gm. and proceed as above. The volume found, multiplied by 2, gives the per cent. of $CaCO_3$.

CITRIC ACID.

$$C_3H_4\ (OH)\ (COOH)_3 + H_2O = 210{\cdot}08.$$

THIS acid in the free state may readily be titrated with normal soda and phenolphthalein. 1 c.c. normal alkali = 0·07 gm. crystallized citric acid.

1. Citrates of the Alkalies and Earths.—These citrates may be treated with neutral solution of lead nitrate or acetate, in the absence of other acids precipitable by lead. The lead citrate is washed with a mixture of equal parts alcohol and water, the precipitate suspended in water, and H_2S passed into it till all the lead is converted into sulphide; the clear liquid is then boiled to remove H_2S, and titrated with normal alkali.

2. Fruit Juices, etc.—If tartaric is present, together with free citric acid, the former is first separated as potassium bitartrate, which can very well be done in the presence of citric acid.

Method of Procedure: A cold saturated solution of potassium acetate in proof spirit is added to a somewhat strong solution of the mixed acids in proof spirit in sufficient quantity to separate all the tartaric acid as bitartrate, the mixture after stirring well being allowed to stand some hours. The precipitate is then transferred to a filter, and washed with proof spirit, then rinsed off the filter with a cold saturated solution of potassium bitartrate, and allowed to stand some hours, with occasional stirring; this treatment removes any adhering citrate. The bitartrate is again brought on to a filter, washed once with proof spirit, then dissolved in hot water, and titrated with normal alkali, 1 c.c. of which =0·15 gm. tartaric acid.

The first filtrate may be titrated for the free citric acid present after evaporating the bulk of the alcohol.

3. Lime and Lemon Juices.—The citric acid contained in lemon, lime, and similar juices, may be very fairly determined by Warington's method.*

Method of Procedure: 15 or 20 c.c. of ordinary juice, or 3–4 c.c. of concentrated juice, are first exactly neutralized with pure normal soda, made up, if necessary, to about 50 c.c., heated to boiling in a salt bath, and so much solution of calcium chloride added as to be slightly in excess of the organic acids present. The mixture is kept at the boiling point for about half an hour, the precipitate collected on a filter and washed with hot water, filtrate and washings concentrated to about 15 c.c., and a drop of ammonia added; this will produce a further precipitate, which is collected separately on a very small filter by help of the previous filtrate, then washed with a small quantity of hot water. Both filters, with their precipitates, are then dried, ignited at a low red heat, and the ash titrated with normal or $^{N}/_{10}$ acid, each c.c. of which represents respectively 0·07 or 0·007 gm. $H_3\overline{Ci} + H_2O$.

FORMIC ACID.

$HCOOH = 46{\cdot}02$.

H. C. Jones† has worked out a method which though not acidimetric may be quoted here. It is based on a process originally devised by Péau de Saint-Gilles, viz., titration with permanganate in the presence of an alkali carbonate. Lieben confirmed this, using a more elaborate process. The method is on the same principle, but the procedure differs from that of Lieben.

Method of Procedure: The solution containing the formic acid is made alkaline with Na_2CO_3, warmed, and an *excess* of standard permanganate added. All the formic acid is thus oxidized, and a precipitate of manganese hydroxide thrown down. The solution is acidified with H_2SO_4, and a measured volume of oxalic acid run in until all the precipitate has dissolved and the permanganate disappeared. The excess of oxalic acid is then titrated with standard permanganate. A volume of oxalic acid equal to that taken is also titrated with the permanganate solution, and the difference between the result and the total permanganate used gives the quantity of permanganate required to oxidize the formic acid. The experimental results agree well among themselves and with those obtained by other methods.

The author further shows that Saint-Gilles' statement that

* *J. C. S.* 1875, 934. † *Amer. Chem. Jour.* **17**, 539-541.

oxalic acid can be titrated in acid solution in the presence of formic acid is unreliable, since formic acid is also oxidized to some extent by the permanganate under these conditions.

F. Freyer*, having occasion to determine the formate in a mixture of calcium acetate and formate, has devised the following method.

METHOD OF PROCEDURE: The mixed calcium salts are distilled with dilute sulphuric acid in a current of steam until the distillate is no longer acid; an aliquot portion of the distillate is titrated with alkali to determine the total acid, whilst another portion is evaporated, if necessary, with excess of caustic soda to concentrate it, and is treated as follows: 10 to 20 c.c., containing about 0·5 gm. of formic acid, are heated for half an hour to an hour with 50 c.c. of a 6 per cent. solution of potassium dichromate and 10 c.c. of concentrated sulphuric acid in a flask provided with a reflux condenser. The liquid is now made up to 200 c.c., and the unaltered chromic acid determined in 10 c.c. of it. For this purpose, 1 to 2 gm. of pure potassium iodide, 10 c.c. of a 25 per cent. solution of phosphoric acid, and some water are added; and after five minutes the solution is diluted to about 100 c.c. with boiled water, and titrated with $^N/_{10}$ thiosulphate solution in the usual manner. The phosphoric acid is added according to Meineke's recommendation, and is for the purpose of rendering the change from the blue colour of the iodide of starch to the green of the chromium salt more visible; the commercial glacial acid may be dissolved in water, oxidized by potassium permanganate until it has a faint rose colour, and filtered before being used.

The dichromate solution used for the oxidation is titrated in the same way. One mol. potassium dichromate is equivalent to three mols. formic acid.

The results quoted by the author show that the method is fairly accurate, both in the absence and in the presence of acetic acid

HYDROFLUORIC ACID, HYDROFLUOSILICIC (SILICO-FLUORIC) ACID, AND FLUORIDES.

1 c.c. of $^N/_1$ alkali $= 0{\cdot}02$ gm. of HF $= 0{\cdot}024$ gm. of H_2SiF_6.

COMMERCIAL hydrofluoric acid is as a rule far from pure. It generally contains hydrofluosilicic acid, sulphuric acid, sulphurous acid, and frequently traces of iron and lead. Two analyses of commercial acid gave the following figures:—

	1	2
Hydrofluoric acid	48·00	45·80
Hydrofluosilicic acid	13·05	9·49
Sulphuric acid	4·07	3·23
Sulphurous acid	0·49	1·06
Left on evaporation	0·16	—
Water by difference	34·23	40·42
	100·00	100·00

If it is desired to prepare pure acid, the best way is to add to the commercial acid peroxide of hydrogen till it ceases to decolorize iodine,

* *Chem. Zeit.* **19**, 1184.

and then potassic hydric fluoride sufficient to fix all the hydrofluosilicic and sulphuric acids. Re-distillation in a lead retort with a platinum condenser will then give perfectly pure acid.

The total amount of free acid may be determined with normal alkali (preferably potash), using phenolphthalein or litmus, the former being best. Methyl orange and lacmoid do not give good results. In the case of pure acid, each c.c. of $^N/_1$ alkali indicates 0·02 gm. of HF, and the reaction when phenolphthalein is employed is very sharp. When, however, commercial acid is thus titrated a difference is observed; the pink colour obtained on adding the alkali only endures for a second or so and then fades away, and this may be repeated for some time till at last a permanent pink is produced. The cause of this is the presence of hydrofluosilicic acid. The first appearance of pink ensues when the reaction $H_2SiF_6 + K_2O = K_2SiF_6 + H_2O$ occurs. Then another reaction sets in

$$K_2SiF_6 + 2K_2O = 6KF + SiO_2,$$

but from the slight solubility of the potassium silicofluoride some time elapses before it is complete.

The sulphuric and sulphurous acids must also be determined if the real amount of HF is required.

Determination of Sulphuric Acid in Presence of Hydrofluoric Acid (W. B. Giles) Long experience has convinced the author of this new process that all methods depending upon the supposed solubility of barium fluoride, and the corresponding insolubility of the sulphate, in either hot or cold diluted hydrochloric acid give most erroneous results. For instance, a sample of hydrofluoric acid known to contain 4 % of H_2SO_4 was treated in the way described by Fresenius, using a large volume of hot dilute hydrochloric acid, and the precipitate was copiously washed with the same weak acid. The barium precipitate obtained was equal to 6·08 % of H_2SO_4 or over 50 % more than was present, and it was found that on repeatedly moistening the precipitate with dilute H_2SO_4, and re-igniting, that the weight increased materially, showing co-precipitation of barium fluoride. The author therefore devised the following process for the determination of the SO_3, which gives accurate results. Its basis is—

1. The conversion of HF into H_2SiF_6, which is easily accomplished.
2. The precipitation of the SO_3 from this solution by means of lead silicofluoride.
3. The total insolubility of $PbSO_4$ in a solution containing an excess of the said lead salt.

Method of Procedure: A convenient weight of the hydrofluoric acid is placed in a platinum dish, about half its volume of water is added, and then precipitated silica in evident excess, and the whole is allowed to stand with occasional stirring for a few hours. It is then filtered, using an ebonite funnel, into another suitable platinum basin, and the excess of silica thoroughly washed. The filtrate and washings are then evaporated to a convenient bulk, and solution of lead silicofluoride is added in excess. If the least trace of sulphuric acid was originally contained in the acid, an almost immediate precipitate of $PbSO_4$ will form, as it is exceedingly insoluble in the presence of the lead silicofluoride. The solution is allowed to stand an hour or two, and the $PbSO_4$ separated by filtration, when it can of course be treated in any convenient volumetric way for the determination of the lead, or it may be weighed direct.

Lead silicofluoride is easily prepared by saturating commercial HF with coarsely powdered flint in a lead basin, and then agitating with powdered litharge. Its solubility is very great, and the specific gravity of the solution may reach 2·000 or more.

EXAMPLE: To 37·89 gm. of chemically pure HF of 1250 sp. gr. there was added 25 c.c. of normal acid ($=1{\cdot}0$ gm. SO_3.) The mixture was then treated as described above, and gave $PbSO_4$ 3·782 gm. $=1{\cdot}0002$ gm. of SO_3.

Determination of the Hydrofluosilicic Acid.—To a convenient quantity of the acid contained in a platinum dish a solution of potassium acetate in strong methylated spirit is added in excess, and then more spirit is added, so that there may be about equal volumes of liquid and spirit. Allow to stand for several hours, and then filter and wash with a mixture of half spirit and half water. The resulting potassium silicofluoride may then be titrated with normal alkali according to the equation:

$$K_2SiF_6 + 2\ K_2O = 6\ KF + SiO_2,$$

or if the filter was a weighed one, it may be dried at 100° C. and weighed direct.

EXAMPLE: 2 gm. of chemically pure precipitated silica were dissolved in a large excess of pure diluted HF. Treated as above described, it yielded 7·35 gm. of K_2SiF_6 which equals 2·004 gm. of silica; 2 gm. of some powdered flint treated in the same way with 50 gm. of pure HF (of 40 %) gave 7·168 gm. of K_2SiF_6 = 1·958 gm. of silica.

Sulphurous Acid.—This is easily determined by taking the solution which results from the total acidity determination and titrating with decinormal iodine. Commercial hydrofluoric acid generally contains from 0·5 to 2·0 %.

The amount of each of the impurities being thus known, the percentage of real HF is easily calculated; *e.g.*, 10 gm. of an acid was found to neutralize 276·0 c.c. of normal alkali. It was found to give the following results:—

c.c. normal alkali 8·0 = 3·23 SO_3
,, ,, ,, 39·0 = 9·36 H_2SiF_6
276 − 47 = 229 c.c. × 0·02 = 45·80 % HF.
41·61 % H_2O by difference

100·00

In this instance the amount of SO_2 was not allowed for.

Bifluorides.—These salts may be titrated in the same way as the acid with phenolphthalein. They generally contain some silicofluoride.*

The determination of fluorine in soluble fluorides has been done volumetrically by Knoblоch†. The process is based on the following facts:—

When a solution of ferric chloride is mixed with its equivalent quantity of potassium fluoride the decomposition is complete, and the resulting ferric fluoride solution is colourless. In this state the iron is not detectable by such tests as thiocyanate, salicylic acid, etc. Still more interesting is the fact that ferric fluoride does not liberate iodine from iodides.

The following standard solutions, etc., are required:—

$^{N}/_{10}$ potassium fluoride; 5·809 gm. of the pure ignited salt in a litre of water.

* The whole of this section, to this point, is kindly contributed by W. B. Giles, F.I.C., who has had large practical experience in the subjects treated.

† *Pharm. Zeitschrift* **39**, 558.

$^{N}/_{60}$ solution of ferric chloride, which the author prepared by diluting 19 gm. of the officinal ferric chloride of the Prussian pharmacopœia to a litre.

$^{N}/_{30}$ sodium thiosulphate solution.

Zinc iodide solution, made by mixing 10 gm. of iodine, 5 gm. of zinc powder, and 25 c.c. of water in a flask, and warming till the violent action is over and the solution colourless, then diluting to 40 c.c. and filtering.

METHOD OF PROCEDURE: The liquid containing the fluorides in solution is mixed with a known excess of ferric chloride solution, then with excess of zinc iodide, and allowed to remain in a closed vessel at 35 – 40° C. for half an hour; the liberated iodine is then titrated with thiosulphate. The volume of the latter used is deducted from that of the ferric chloride—the difference being the measure of the fluorine. 1 c.c. thiosulphate = 0·0019 gm. F.

The author states that calcium and strontium in their soluble salts may also be determined by the same method by acidifying their solutions with hydrochloric acid, adding equal volumes, first of potassium fluoride and then of ferric chloride solution in excess, adding excess of zinc iodide, and digesting at 35 – 40° C. The liberated iodine is ascertained as before. 1 c.c. of thiosulphate = 0·002 Ca.

None of these reactions have been verfied by me, but the method as given here is novel, and probably capable of being developed with further experience.

A very interesting paper on the acidimetry of hydrofluoric acid is contributed by Haga and Osaka*, being the results of independent experiments made by them in the laboratory of the Imperial University, Japan.

The authors examined the behaviour of the usual indicators in the neutralization of hydrofluoric acid. That its alkali salts blue litmus and that its avidity number places it among the vegetable acids rather than with the strong mineral acids, appear to be the only two facts yet recorded bearing upon its acidimetry.

To get uniform indications it was found necessary to have not only the acid pure, but the titrating solutions also; a little silica, alumina, or carbon dioxide affecting the titration more than it would in the case of the ordinary mineral acids.

Phenolphthalein is the best indicator, and leaves nothing to be desired when potash or soda is used for the titration. Rosolic acid is almost equal to it, and can be used also with ammonia. With both indicators the change of colour has the advantage of being very evident in platinum vessels. Methyl orange is useless. Litmus, lacmoid and phenacetolin are all capable of being made to yield accurate results in the hands of an experienced operator.

The fact that accurate results can only be obtained with very pure acids and reagents militates against the value of any acidimetric process, and therefore the indirect method by Giles, described above, is of greater technical value.

* *J. C. S.* **17**, **18**, 251.

OXALIC ACID.

$C_2H_2O_42H_2O = 126·05.$

THE free acid can be accurately titrated with normal alkali and phenolphthalein.

PROCEDURE WHEN IN COMBINATION WITH ALKALIES: The acid can be precipitated with calcium chloride as calcium oxalate, where no other matters precipitable by calcium are present. If acetic acid is present in slight excess it is of no consequence, as it prevents the precipitation of small quantities of sulphates. The precipitate is well washed, dried, ignited, and the carbonate titrated with normal acid, 1 c.c of which = 0·063 gm. $\overline{O}$.

Acid oxalates are titrated direct for the amount of free acid. The reaction continues to be acid until alkali is added in such proportion that 1 molecule acid = 2 atoms alkali metal.

The combined acid may be found by igniting the salt, and titrating the residual alkaline carbonate as above.

PHOSPHORIC ACID.

$P_2O_5 = 142·08.$

Thomson has shown in his researches on the indicators that phosphoric acid, either in the free state or in combination with soda or potash, may with very fair accuracy be determined by the help of methyl orange or phenolphthalein. If, for instance, normal potash be added to a solution of phosphoric acid until the pink colour of methyl orange is discharged, KH_2PO_4 is formed (112 KHO = 142 P_2O_5.) If now phenolphthalein is added, and the addition of potash continued until a red colour appears, K_2HPO_4 is formed. (Again 112 KHO = 142 P_2O_5.) On adding standard hydrochloric or sulphuric acid until the pink colour of methyl orange reappears, the titration with standard potash may be repeated. In each case 1 c.c. normal potash = ·071 gm. P_2O_5 or ·098 gm. H_3PO_4, each titration acting as a check upon the others.

Or the titration may be made with phenolphthalein only. But to obtain a sharp end-reaction the standard alkali must be free from carbonate and the solution should be cold and concentrated (preferably with the addition of sodium chloride), in order to prevent dissociation of the dibasic salt formed, whereby it tends to react alkaline to the indicator. $H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O$. 1 c.c. normal alkali = ·0355 gm. P_2O_5 or ·049 gm. H_3PO_4.

Many attempts have been made to utilize these reactions for the accurate determination of P_2O_5 in manures, etc., but, so far as my experience goes, without adequate success.

Titration as Ammonio-magnesium Phosphate.—Stolba* adopts an alkalimetric method, which depends upon the fact that one molecule of the double salt requires two molecules of a mineral acid for saturation.

* *Chem. Cent.* 1866, 727, 728.

METHOD OF PROCEDURE: The precipitation is made with magnesia mixture, the precipitate well washed with ammonia, and the latter completely removed by washing with alcohol of 50 or 60 per cent. The precipitate is then dissolved in a measured excess of $^N/_{10}$ acid, methyl orange added, and the amount of acid required found by titration with $^N/_{10}$ alkali. Care must be taken that all free ammonia is removed from the filter and precipitate, and that the whole of the double salt is decomposed by the acid before titration, which may always be ensured by using a rather large excess and warming. The titration is carried out in the cold.

This method has given me very good results in comparison with the gravimetric method. The same method is applicable to the determination of arsenic acid, and also of magnesia.

$$\begin{aligned} 1 \text{ c.c. of } ^N/_{10} \text{ acid} &= 0{\cdot}00355 \text{ gm. } P_2O_5 \\ ,, \quad ,, \quad &= 0{\cdot}00575 \text{ gm. } As_2O_3 \\ ,, \quad ,, \quad &= 0{\cdot}002 \text{ gm. } MgO \end{aligned}$$

The reaction in the case of phosphoric acid may be expressed as follows:—

$$Mg\,(NH_4)\,PO_4 + 2HCl = (NH_4)\,H_2PO_4 + MgCl_2.$$

Determination of Phosphoric Acid in its Pure Solutions.—R. Segalle* has investigated various methods for the above purpose with the following result:—

By far the most accurate results are obtained by Glücksmann's method. In this, the phosphoric acid is precipitated by an excess of magnesia mixture of known strength in free ammonia, the precipitate filtered off, and the free ammonia left in solution is titrated by standard acid. From the equation—

$$H_3PO_4 + MgSO_4 + 3NH_3 = MgNH_4PO_4 + (NH_4)_2SO_4$$

it will be seen that $H_3PO_4 = 3NH_3$.

The following modification is recommended as being more convenient and simple. To the phosphoric acid solution, contained in a graduated flask, an excess of standard ammonia (preferably normal) is added, followed by an excess of a saturated neutral solution of magnesium sulphate. The liquid is then diluted to the mark, well shaken, and filtered, and the residual ammonia titrated in an aliquot part of the filtrate. "Methyl red" (see p. 41) is especially suitable as indicator in this process, as in ammonia titrations of all kinds.

On account of its simplicity, the modified method is well adapted for ascertaining the strength of the solutions of phosphoric acid employed in pharmacy

J. M. Wilkie† has devised a method for the direct titration of free tri-basic phosphoric acid in the same manner as other acids. To the phosphoric acid solution is added silver nitrate and sodium acetate, and the liberated acetic acid is titrated with standard baryta in the presence of phenolphthalein.

From the equation,

$$H_3PO_4 + 3\,AgNO_3 + 3\,CH_3COONa = Ag_3PO_4 + 3NaNO_3 + 3CH_3COOH$$

it is seen that $H_3PO_4 = 3CH_3COOH$.

METHOD OF PROCEDURE: A suitable amount of the free acid is diluted to about 50 c.c., excess of approximately decinormal silver nitrate is then added and finally a large excess of 3 % sodium acetate. After adding a few drops of phenolphthalein, baryta is run in until a permanent pink coloration is developed.

$$\begin{aligned} 1 \text{ c.c. } ^N/_{10}\text{ Ba}\,(OH)_2 &= 0{\cdot}00327 \text{ gr. } H_3PO_4 \\ &= 0{\cdot}00237 \text{ gr. } P_2O_5. \end{aligned}$$

* *Z. a. C.* **34**, 33-39. † *J. S. C. I.* 1909, 68.

Unless an excessive amount of silver is added the end point is sharp and easy of recognition, since the precipitated silver phosphate readily settles leaving the supernatant liquid nearly clear. The method is also available for the mono- and di-alkali phosphates (ammonium if present must be removed by evaporation or boiling with standard alkali), but in the presence of alkali carbonate it is necessary also to determine the amount of silver actually precipitated as silver phosphate.* (See under Phosphoric Acid and Phosphates).

For example, if a weight w of Na_2HPO_4 requires b. c.c. $^N/_{10}$ $Ba(OH)_2$ and a c.c. $^N/_{10}$ $AgNO_3$, we have

$$\% \ Na_2CO_3 = \frac{(a - 3b) \ 0{\cdot}177}{w}$$

$$\% \ Na_2HPO_4 = \frac{a \times 0{\cdot}473}{w}$$

or in terms of P_2O_5 and total Na_2O.

$$\% \ P_2O_5 = \frac{a \times 0{\cdot}237}{w}$$

$$\% \ Na_2O = \frac{(a - b) \ 0{\cdot}31}{w}$$

Precautions.—All water used must be free from CO_2. In the case of Na_2HPO_4 it is necessary to free from CO_2 by boiling with at least sufficient standard acid to convert to NaH_2PO_4, due allowance being made in the baryta titration. The silver nitrate should be tested for neutrality by treating with excess of sodium chloride and then adding phenolphthalein and one drop of $^N/_{10}$ NaOH. The sodium acetate likewise must be neutral and free from carbon dioxide. Alkali chloride if present has no effect in the baryta-titration but must be allowed for in the silver-titration.

Other methods are described under Phosphoric Acid and Phosphates.

FUMING SULPHURIC ACID.

Nordhausen Oil of Vitriol.

This consists of a mixture of SO_3 and H_2SO_4. When rich in SO_3 it exists in a solid form, and being very hygroscopic cannot be weighed in the ordinary manner. Accordingly, it is weighed either in glass bulbs or in a Lunge and Rey's glass-tap pipette. The bulbs used for this purpose are of about 2 c.m. diameter, with two capillary tubes fused in. The acid, if solid, is first melted and when quite homogeneous is sucked up into the bulb by means of an indiarubber tube attached to one capillary tube, the other being dipped in the acid. About 3-5 gm. are taken and the bulb should be about half-filled. The wet tube is carefully cleaned outside, and one of the capillary ends is sealed. The bulb is then weighed, best by supporting it on a platinum crucible with two nicks, on which the ends of the bulb rest. In case of fracture, the acid runs into the crucible instead of on the balance. When weighed, put the bulb, open end downward, into a small conical flask, into the neck of which it fits exactly, and containing sufficient water to cover well the lower part of the tube. Break off the other point, allow the acid to run out, blow a few drops of water into the upper capillary,

* *J. S. C. I.* 1910, 794.

and finally rinse the whole bulb tube by repeated aspiration of water. Dilute the liquid to 500 c.c. and titrate 50 c.c. of it with $^N/_5$ sodium carbonate solution, using methyl orange as indicator. From the acidity thus found must be deducted that due to SO_2, which is determined by titrating another portion with $^N/_{10}$ Iodine. For each c.c. of the latter 0·05 c.c. normal sodium carbonate is subtracted, since with methyl orange the colour changes when SO_2 has passed into $NaHSO_3$.

Let n = no. of c.c. of sodium carbonate used,
m = ,, ,, $^N/_{10}$ iodine solution required for the same quantity of acid,
the acidity due to $H_2SO_4 + SO_3$ is

$$(n - 0{\cdot}05\ m) \times 0{\cdot}040035 \text{ in terms of } SO_3.$$

To the SO_3 thus found add the SO_2 (calculated = 0·0032035 m) and assume the residue, in the absence of solid impurities, to be water. By multiplying this water by 4·443 we obtain the quantity of SO_3 combined with it to form H_2SO_4, and by deducting this from the total acidity that of the *free* SO_3.

TARTARIC ACID.

$C_4H_6O_6 = 150{\cdot}05$ (Dibasic.)

The free acid may be readily titrated with normal alkali and phenolphthalein.

1 c.c. normal alkali = 0·075 gm. tartaric acid.

The amount of tartaric acid existing in tartaric acid liquors is best determined by precipitation as potassium bitartrate ; the same is also the case with crude argols, lees, etc. Manufacturers are indebted to Warington and Grosjean for most exhaustive papers on this subject, to which reference should be made by all who desire to study the nature and analysis of all commercial compounds of citric and tartaric acids.*

Without entering into the copious details and explanations given by these authorities, the methods may be summarized as follows :—

Commercial Tartrates.

In the case of good clean tartars, even though they may contain sulphates and carbonates, accurate results may be obtained by indirect methods.

(*a*) The very finely powdered sample is first titrated with normal alkali, and thus the amount of tartaric acid existing as bitartrate is found ; another portion of the sample is then calcined at a moderate heat, and the ash titrated. By deducting from the volume of acid so used the volume used for bitartrate, the amount of base corresponding to neutral tartrates is obtained.

(*b*) The whole of the tartaric acid is exactly neutralized with caustic soda, evaporated to dryness, calcined, and the ash titrated with normal acid ; the total

* Warington, *J.C.S.* 1875, 925-994 ; Grosjean, *J.C.S.* 1879, 341-356.

tartaric acid is then calculated from the volume of standard acid used ; any other organic acid present will naturally be included in this amount. In the case of fairly pure tartars, etc., this probable error may be disregarded

METHOD OF PROCEDURE : 5 gm. of the finely powdered tartar are heated with a little water to dissolve any carbonates that may be present. If it is wished to guard against crystalline carbonates, 5 c.c. of standard HCl are added in the first instance, and the heating is conducted in a covered beaker. Standard alkali is next added to the extent of about three-fourths of the amount required by a good tartar of the kind examined, plus that equivalent to the acid used, and the whole is brought to boiling : when nearly cold, the titration is finished. From the amount of alkali consumed, minus that required by the HCl, the tartaric acid present as acid tartrate is calculated.

2 gm. of the powdered tartar are next weighed into a platinum crucible with a well-fitting lid ; the crucible is placed over an argand burner ; heat is applied, very gently at first, to dry the tartar, and then more strongly till inflammable gas ceases to be evolved. The heat should not rise above very low redness. The black ash is next removed with water to a beaker. If the tartar is known to be a good one, 20 c.c. of standard H_2SO_4 are now run from a pipette into the beaker, a portion of the acid being used to rinse the crucible. The contents of the beaker are now brought to boiling, filtered, and the free acid determined with standard alkali. As the charcoal on the filter under some circumstances retains a little acid, even when well washed, it is advisable when the titration is completed to transfer the filter and its contents to the neutralized fluid, and add a further amount of alkali if necessary. From the neutralizing power of a gram of burnt tartar is subtracted the acidity of a gram of unburnt tartar, both expressed in c.c. of standard alkali, the difference is the neutralizing power of the bases existing as neutral tartrates, and is then calculated into tartaric acid on this assumption.*

If the tartar is of low quality, 5 c.c. of solution of hydrogen peroxide (1 volume =10 volumes O_2) are added to the black ash and water, and immediately afterwards the standard acid ; the rest of the analysis proceeds as already described ; the small acidity usually belonging to the peroxide solution must, however, be known and allowed for in the calculation. By the use of hydrogen peroxide the sulphides formed during ignition are reconverted into sulphates, and the error of excess which their presence would occasion is avoided.

The above method does not give the separate amounts of acid and neutral tartrates in the presence of carbonates, but it gives the correct amount of tartaric acid ; it is also correct in cases where free tartaric acid exists, so long as the final results show that some acid existed as neutral salt. Whenever this method shows that the acidity of the original substance is greater than the neutralizing power of the ash, it will be necessary to use the method *b*, which is the only one capable of giving good results when the sample contains much free tartaric acid.

Methods adopted by the Seventh International Congress of Applied Chemistry, London, 1909.†

The crude tartrate should be carefully sampled, ground, and passed through a sieve having a mesh of 0·5 mm.

* It is obvious that the neutralizing power of the ash of an acid tartrate is exactly the same as the acidity of the same tartrate before burning. In making the calculations, it must be remembered that the value of the alkali in tartaric acid is twice as great in the calculation made from the acidity of the unburnt tartar as in the calculation of the acid existing as neutral tartrates.

† P. Carles, *Ann. Chim. analyt.*, 1910, **15**, 231.

DETERMINATION OF THE BITARTRATE.—A weighed portion of 2·35 gm. of the sample is boiled for 5 minutes with 400 c.c. of water in a 500 c.c. flask, then cooled, diluted to the mark, mixed and filtered ; 250 c.c. of the filtrate are heated to boiling, and titrated with $^{N}/_{4}$ potassium hydroxide solution, using litmus paper as indicator. The potassium hydroxide solution is standardized under the same conditions with pure potassium bitartrate.

DETERMINATION OF TOTAL TARTARIC ACID.—In cases of tartrates containing upwards of 45 per cent. of total tartaric acid, 6 gm. of the sample are taken for the determination ; where the tartaric acid falls below 45 per cent., 12 gm. of the sample are used, this quantity being also taken for the analysis of calcium tartrates. The weighed portion of the sample is thoroughly mixed with 18 c.c. of hydrochloric acid of sp. gr. 1·1 ; after the lapse of 15 minutes, the mixture is rinsed into a 200 c.c. flask with water and diluted to the mark. The solution is then poured through a filter, 100 c.c. of the filtrate are heated to boiling and 10 c.c. of 66 per cent. potassium carbonate solution are added slowly. The mixture is heated for about 20 minutes and the liquid together with the precipitate is transferred to a 200 c.c. flask, cooled, and diluted to volume. After filtering, 100 c.c. of the filtrate are evaporated to a volume of 15 c.c., 3·5 c.c. of glacial acetic acid are added, drop by drop, and the mixture is stirred for 5 minutes ; at the end of 10 minutes, 100 c.c. of 95 per cent. alcohol are added, the stirring is continued for 5 minutes, and, after the lapse of a further 10 minutes, the liquid portion is poured through a filter, the precipitate is washed three or four times by decantation with a little alcohol, then brought on to the filter and washed with alcohol until the washings are free from acidity. The filter together with the precipitate is then placed in a flask, boiled with 300 c.c. of water for 1 minute, and the hot solution titrated with $^{N}/_{4}$ potassium hydroxide solution, using litmus paper as indicator. The following corrections are made for the volume of the insoluble matter :—For tartrates containing 20 per cent. of total tartaric acid, 0·8 is deducted from the total percentage of acid found ; for 30 per cent. tartrates, 0·70, and for 40 per cent. tartrates, 0·6. In the case of tartrates containing 50, 60, and 80 per cent. of tartaric acid, 0·25, 0·15, and 0·1 per cent. is deducted respectively.

Cream of Tartar.

When prepared by boiling crude tartar or " argol " with water, filtering, and crystallizing the salt from the clear liquid, cream of tartar always contains more or less calcium tartrate, which, though nearly insoluble in cold water, dissolves with moderate facility in a hot solution of acid tartrate of potassium. From experiments made, as well as from numerous analyses, Allen* concluded that the commercial article should not contain more than 9 or 10 per cent. of calcium tartrate. After a consideration of possible impurities, he recommended the following process :—

1. Dissolve 1·881 gm. of the moisture-free sample in hot water and titrate with $^{N}/_{10}$ caustic alkali and phenolphthalein. In the absence of acid potassium sulphate (and of free tartaric acid) each c.c. of alkali required represents 1 per cent. of acid potassium tartrate in the sample.

2. Ignite 1·881 gm. of the moisture-free sample at a dull red heat for 10 minutes, without attempting to burn off all the carbon. Boil the product with water, filter, and wash the insoluble carbonaceous residue.

* On the composition and analysis of commercial cream of tartar, *The Analyst*, 1896, **21**, 174 and 209.

(*a*) Titrate the filtrate with $^N/_{10}$ HCl and methyl-orange. In a pure sample the volume of acid required will exactly equal that of the alkali consumed in process 1. The presence of calcium tartrate in the sample does not affect the results. Each c.c. of *deficiency* of acid represents 0·36 per cent of calcium sulphate ($CaSO_4$), or 0·72 per cent. of $KHSO_4$. Any *excess* of acid required points to the presence of neutral potassium tartrate, each c.c. of difference representing 0·60 per cent of that salt.

(*b*) Ignite the carbonaceous residue, dissolve in 20 c.c. of $^N/_{10}$ acid, filter if necessary, wash, and titrate the filtrate with $^N/_{10}$ alkali and methyl-orange. Each c.c. required corresponds to 0·50 per cent. of calcium tartrate or 0·36 per cent. of $CaSO_4$.

PART III.

ANALYSIS BY OXIDATION OR REDUCTION.

THE number of methods of analysis based on oxidation or reduction is very great, and not a few of them possess extreme accuracy, such accuracy, in fact, as it is not possible to attain by any gravimetric method. The completion of the various processes is generally shown by a distinct change of colour, *e.g.*, the beautiful rose-red tint of permanganate and the blue colour of iodide of starch: and as the smallest quantity of these substances suffices to colour distinctly large volumes of liquid, the slightest excess of the oxidizing agent is sufficient to produce a distinct effect.

The principle involved in the process is extremely simple. Substances having a strong affinity for oxygen are brought into solution, and titrated with an oxidizing solution of known strength. For example, ferrous salts rapidly absorb oxygen, and when a solution of permanganate is gradually added to a solution of a ferrous salt the latter instantly discharges the colour of the drops at first run in, but after the whole of the ferrous salt has been converted into the ferric state the liquid becomes rose-coloured on the further addition of a few drops of permanganate, the appearance of this colour indicating the completion of the change. The reaction is, in its simplest form, as follows:—

$$10FeO + K_2Mn_2O_8 = 5Fe_2O_3 + 2MnO + K_2O.$$

The titration is carried out in the presence of dilute sulphuric acid, and sulphates are formed. Similarly, oxalic acid, in the presence of sulphuric acid, is readily oxidized by permanganate, carbon dioxide being formed. The reaction is:—

$$5H_2C_2O_4 + K_2Mn_2O_8 + 3H_2SO_4 = 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Here, again, the appearance of a rose tint in the solution shows that the oxidation is complete.

The strength of many oxidizing agents is determined by adding a known quantity of a reducing agent in excess, then ascertaining the amount of this excess by residual titration with a standard oxidizing solution. The strength of the reducing solution being known, the quantity required is a measure of the substance which has been reduced by it.

The oxidizing agents frequently used are potassium permanganate, iodine, potassium dichromate, and potassium ferricyanide.

The reducing agents employed are sulphurous acid, sodium hyposulphite (Schützenberger's), sodium thiosulphate, oxalic acid, ferrous salts, arsenious oxide, stannous chloride, potassium ferrocyanide, zinc and magnesium. Titanium chloride, a very powerful reducing agent, will be referred to later.

The most commonly used combinations of the above are :—

1. Permanganate and ferrous salts : permanganate and oxalic acid. Both used in sulphuric acid solution, the appearance of a rose colour being the indicator.

2. Potassium dichromate and ferrous salts, with potassium ferricyanide as indicator.

3. Iodine and sodium thiosulphate ; iodine and sodium arsenite, with starch as indicator in each case.

PREPARATION OF STANDARD SOLUTIONS.

PERMANGANIC ACID AND FERROUS OXIDE.

1. Potassium Permanganate.

$K_2Mn_2O_8 = 316 \cdot 06$. Decinormal Solution $= 3 \cdot 161$ gm. per litre.

1 c.c. $= 0 \cdot 0008$ gram Oxygen.

THE solution of this salt is best prepared for analysis by dissolving the pure crystals in freshly distilled water, and should be of such a strength that 17·9 c.c. will oxidize 1 decigram of iron. The solution is then decinormal. If the salt can be had perfectly pure and dry, 3·161 gm. dissolved in a litre of water at 15° C. will give an exactly decinormal solution ; but, nevertheless, it is always well to verify it as described below. Fairly pure permanganate, in large crystals, may now be obtained in commerce, and if this salt is recrystallized twice from hot distilled water and dried thoroughly at 100° C., it will be found practically pure. If kept in the light in ordinary bottles it will retain its strength for several months, if in bottles covered with black paper much longer; nevertheless, it should from time to time be verified by titration in one of the following ways :—

2. Titration of Permanganate.

(*a*) **With Metallic Iron.**—There is no difficulty in obtaining iron of 99·8 per cent. purity. It is sold in the form of thin wire, each piece of which should be drawn between two pieces of fine emery cloth and then wiped with a dry cloth before use; this treatment removes rust.

METHOD OF PROCEDURE: Fit a tight cork or rubber stopper, with bent delivery tube, into a flask holding about 300 c.c., and clamp it in a retort stand in an inclined position, the tube being so bent as to dip into a small beaker containing pure water. Fill the flask one-third with pure dilute sulphuric acid, and add a few grains of sodium carbonate in crystals ; the CO_2 so produced will drive out the air. While this is being done weigh about 0·1 gram of the wire ; put it quickly into the flask when the soda is dissolved, and apply a gentle heat till the iron is completely in solution ; a few black specks of carbon are of no consequence. The flask is then rapidly cooled under a stream of cold water, diluted if necessary with some recently boiled and cooled water, and the permanganate run in cautiously from a tap burette, with constant shaking, until a faint rose-colour

permanent. Instead of this arrangement for dissolving the iron the apparatus shown in fig. 44, may be used.

The decomposition which ensues from titrating ferrous oxide by permanganic acid may be represented as follows :—

$$10FeO \text{ and } Mn_2O_7 = 2MnO \text{ and } 5Fe_2O_3.$$

The weight of wire taken, multiplied by 0·998, will give the actual weight of pure iron upon which to calculate the strength of the permanganate.

(*b*) **With Ferrous-ammonium Sulphate.**—In order to ascertain the strength of the permanganate, it may be titrated with a weighed quantity of this substance instead of metallic iron.

This salt is a convenient one for titrating the permanganate, as it saves the time and trouble of dissolving the iron, and when perfectly pure it can be depended on without risk. To prepare it, 139 parts of the purest crystals of ferrous sulphate, and 66 parts of pure crystallized ammonium sulphate are separately dissolved in the least possible quantity of distilled water at about 40° C. (if the solutions are not perfectly clear they must be filtered); mix them at the same temperature in a porcelain dish, adding a few drops of pure sulphuric acid, and stir till cold. During the stirring the double salt will fall in a finely granulated form. Set aside for a few hours, then pour off the supernatant liquid, and empty the salt into a clean funnel with a little cotton wool stuffed into the neck, so that the mother-liquor may drain away; the salt may then be quickly and repeatedly pressed between fresh sheets of clean filtering paper. Lastly, place in a current of air to dry thoroughly, so that the small grains adhere no longer to each other, or to the paper in which they are contained, then preserve in a stoppered bottle for use. This salt is useful for many purposes, and should be made by the analyst himself, as it is difficult to buy the pure ferrous salt. Only a few ounces should be made at a time, according to the directions above, as if large quantities are made it is difficult to dry the granular salt in a purely ferrous state.

The formula of the salt is—$Fe\ (NH_4)_2\ (SO_4)_2,\ 6H_2O = 392{\cdot}17$. Consequently it contains almost exactly one-seventh of its weight of iron; 0·7022 gm. represents 0·1 gm. Fe, and this is a convenient quantity to weigh for the purpose of titrating the permanganate.

METHOD OF PROCEDURE: 0·7022 gm. being brought into dilute cold solution in a flask or beaker, and 20 c.c. of dilute sulphuric acid (1 to 5) added (the titration of permanganate, or any other substance by it, should always take place in the presence of free acid, and preferably sulphuric), the permanganate is delivered from a burette with glass tap, as before described, until a point occurs when the rose colour no longer disappears on shaking.

(*c*) **With Oxalic Acid.**—This is a very quick method of titrating permanganate, if the exact value of the solution of pure oxalic acid is known. 10 c.c. of normal solution are brought into a flask with dilute sulphuric acid, as in the case of the iron salt, and considerably diluted with water, then warmed to about 60° C., and the permanganate added from the burette. The colour disappears slowly at first, but afterwards more rapidly, becoming first brown, then yellow, and so on to colourless. More care must be exercised in this case than in the titration with iron, as the action is not momentary. 100 c.c. should be required to be strictly decinormal. The chemical change which occurs is explained on p. 121.

(*d*) **With Sodium Oxalate.**—The method of titration is the same as with oxalic acid, but is preferable since the salt may easily be obtained pure, and being

anhydrous may be weighed with great exactness. A decinormal solution may be made by dissolving 6·7 gm. per litre. This is one of the best methods of ascertaining the exact strength of permanganate.

3. Precautions in Titrating with Permanganate.

It must be borne in mind that free acid is always necessary in titrating a substance with permanganate, in order to keep the resulting manganous oxide in solution. Sulphuric acid, in a dilute form, has no prejudicial effect on the pure permanganate, even at a high temperature. With hydrochloric acid the solution to be titrated must be very dilute and at a low temperature, otherwise chlorine will be liberated and the analysis spoiled. This acid acts as a reducing agent on permanganate in concentrated solution, thus—

$$Mn_2O_7 + 14HCl = 7H_2O + 5Cl_2 + 2MnCl_2.$$

The irregularities due to this reaction may be entirely obviated by the addition of a few grams of manganous or ammonium sulphate before the titration, which must be performed *slowly*.

In spite of the manifest advantages of standard dichromate where there are reasons for titrating iron in hydrochloric acid solution, many attempts have been made to work out a method with permanganate which shall be accurate and reliable under practical conditions.* For details of some of these methods see under Iron.

Organic matter of any kind decomposes the permanganate, and the solution therefore cannot be filtered through paper, nor can it be used in a clip burette, because it is decomposed by the india-rubber tube. It may, however, be filtered through gun cotton or glass wool.

TITRATION OF FERRIC SALTS BY PERMANGANATE.

All ferric compounds requiring to be determined by permanganate must, of course, be reduced to the ferrous state. This is best accomplished by metallic zinc or magnesium in sulphuric acid solution. Hydrochloric acid may also be used with the precautions mentioned.

The reduction occurs on simply adding to the warm diluted solution small pieces of zinc (free from iron, or at least with a known quantity present) or coarsely powdered magnesium until colourless ; or until a drop of the solution brought in contact with a drop of potassium thiocyanate produces no red colour. All the zinc or magnesium must be dissolved previous to the titration.

The reduction may be hastened considerably as shown under Iron 2.

When the reduction is complete, no time should be lost in titrating the solution.

* Fresenius, *Zeit. Anal. Chem.*, 1862, 361; Zimmermann, *Annalen*, 1882, 305; Reinhardt, *Chem. Zeit.*, 1889, 323; Brandt, *Chem. Zeit.*, 1908, 812, etc.; Friend, *Chem. Soc. Trans.*, 1909, **95**, 1228; Jones and Jeffery, *Analyst*, 1909, **34**, 306.

CALCULATION OF THE RESULTS OF ANALYSES MADE WITH PERMANGANATE SOLUTION.

THE calculation of the results of analyses with permanganate, if the solution is not strictly decinormal, may be made by ascertaining its coefficient, reducing the number of c.c. used for it to decinormal strength, and multiplying the number of c.c. thus found by $\frac{1}{10000}$ of the equivalent weight of the substance sought; for instance—

Suppose that 15 c.c. of permanganate solution have been found to equal 0·1 gm. iron; it is required to reduce the 15 c.c. to decinormal strength, which would require 1000 c.c. of permanganate to every 5·585 gm. iron, therefore $5·585 : 1000 :: 0·1 : x = 17·9$ c.c.; $17·9 \times 0·005585 = 0·09997$ gm. iron, which is as near to 0·1 gm. as can be required. Or the coefficient necessary to reduce the number of c.c. used may be found as follows:—$0·1 : 15 :: 5·585 : x = 83·8$ c.c., therefore $\frac{100}{83·8} = 1·194$. Consequently 1·194 is the coefficient by which to reduce the number of c.c. of that special permanganate to decinormal strength, whence the weight of substance sought may be found in the usual way.

Another plan is to find the quantity of iron or oxalic acid represented by the permanganate used in any given analysis, and this being done the following simple equation gives the required result:—

Fe (55·85) or $\bar{O}$ (63)	:	eq. weight of the substance sought	: :	the weight of Fe or $\bar{O}$ found	:	the weight of substance sought

In other words, if the equivalent weight of the substance analyzed be divided by 55·85 or 63 (the respective equivalent weights of iron or oxalic acid), a coefficient is obtained by which to multiply the weight of iron or oxalic acid equal to the permanganate used, and the product is the weight of the substance titrated.

For example: sulphuretted hydrogen is the substance sought, the eq. weight of H_2S corresponding to 2 eq. Fe is 17·04; let this number be divided by 55·85; $\frac{17·04}{55·85} = 0·3051$; therefore, if the quantity of iron represented by the permanganate used in a determination of H_2S be multiplied by 0·3051, the product will be the weight of the sulphuretted hydrogen sought.

Again: in the case of manganese peroxide, of which the equivalent weight is 43·46;

$$\frac{43·46}{55·85} = 0·7782$$

The weight of iron, therefore, found by permanganate in any analysis multiplied by the coefficient 0·7782 will give the amount of peroxide MnO_2. Again: if m gm. iron $= k$ c.c. permanganate, then

1 c.c. permanganate $=\frac{m}{k}$ gm. metallic iron.

The equivalents here given are on the hydrogen scale, in accordance with the normal system of solutions adopted ; and thus it is seen that two equivalents of iron are converted from the ferrous to the ferric state by the same quantity of oxygen as suffices to oxidize one equivalent of oxalic acid, sulphuretted hydrogen, or manganese peroxide.

1 c.c. decinormal permanganate is equivalent to

0·005585	gm.	Fe determined in the ferrous state			
0·007185	,,	FeO	,,	,,	,,
0·008	,,	Fe_2O_3	,,	,,	,,
0·003733	,,	Fe	,,	from FeS	
0·00595	,,	Sn	,,	,,	$SnCl_2$
0·00298	,,	Sn	,,	,,	SnS_2
0·00318	,,	Cu determined from CuS			
0·00275	,,	Mn	,,	,,	MnS
0·00318	,,	Cu	,,	,,	$Cu + Fe_2Cl_6$
0·00636	,,	Cu	,,	,,	$CuO + Fe$
0·0017	,,	H_2S			
0·0008	,,	$\underline{O}$			
0·0063	,,	O			
0·002	,,	Ca from CaC_2O_4			
0·0120	,,	Ur	,,	UrO, etc., etc.	

When possible, the necessary coefficients will be given in the tables preceding any leading substance.

DETERMINATION OF FERROUS OXIDE BY POTASSIUM DICHROMATE.

(Penny's Method.)

Potassium dichromate, as a reagent for the determination of ferrous iron, possesses the advantages over permanganate that it may easily be obtained in the purest state, it is absolutely permanent in solution, and its solution may be used in a Mohr's burette. On the other hand, the end of the reaction can only be ascertained by means of an external indicator. For this purpose a *freshly-made* and very dilute solution of potassium ferricyanide is spotted on a white tile and drops of the ferrous solution are from time to time brought into contact with the spots of the indicator. At first a deep-blue colour is produced where the drops meet, but as the addition of dichromate is continued this gives place to a bluish-green, then green, shade, and the titration is completed when a drop of the iron solution placed on the tile appears of the same colour as that of the mixed drops of solution and ferricyanide.

The reaction may be simply expressed as follows :—

$$2\ CrO_3 + 6FeO = Cr_2O_3 + 3Fe_2O_3.$$

The decomposition takes place immediately, and at ordinary temperatures, in the presence of free hydrochloric or sulphuric acid. Nitric acid is, of course, inadmissible.

The reduction of ferric compounds to the ferrous state may be effected by stannous chloride, sodium sulphite, ammonium bisulphite, sulphurous acid, or magnesium. Zinc is not so good for this purpose, as the zinc ferricyanide somewhat obscures the end-reaction. In the analysis of iron ores stannous chloride is most useful, as it very rapidly reduces the ferric salt and causes the yellow colour to disappear almost immediately. The reduction is carried out as follows :—

The hydrochloric acid solution of iron, containing a large excess of free acid, is heated to boiling in a flask and fairly strong stannous chloride solution dropped into it from a burette* or a dropping tube till the yellow colour of the solution has nearly gone. The reduction is then finished by adding a more dilute solution of stannous chloride a drop at a time, with agitation of the liquid after each addition, till the last trace of colour has disappeared. A good operator can do this with the greatest accuracy. But as any stannous chloride added in excess of the amount required to reduce the whole of the ferric salt present would reduce the dichromate afterwards run in and so give a high result, the following procedure may be adopted. The reduced solution is poured into a beaker, diluted with water that has been boiled and cooled, and some mercuric chloride solution added. This converts any stannous chloride into the stannic compound with the precipitation of mercurous chloride, which does not interfere with the titration.

For the analysis of iron ores it is most convenient to take 0·5 gram for the analysis, and to use a solution of dichromate containing exactly 4·390 grams of the pure crystals per litre. 1 c.c. = 0·005 gram Fe, and the number of c.c. used in each determination gives the percentage of iron present without any calculation.†

1. Preparation of the Decinormal Solution of Potassium Dichromate.

4·903 grm. per litre.

From the equation

$$6FeO + K_2Cr_2O_7 = 3Fe_2O_3 + Cr_2O_3 + K_2O$$

we see that each molecule of potassium dichromate gives up 3 atoms of oxygen, equivalent to 6 atoms of hydrogen. Hence, as the molecular weight is 294·2, one-sixth of this in grams is equivalent to one gram of hydrogen. In other words, a normal solution contains 49·033 grams per litre. For most purposes, however, a decinormal solution, containing 4·903 grams per litre, is more useful and is the one generally employed.

1 c.c. = 0·0008 gram Oxygen.

* It is best to keep one for the purpose, as the solution gradually marks the glass.

† The weighed portion of an iron-ore should be ignited, gently at first, in a platinum crucible previous to being dissolved in hydrochloric acid, in order to destroy all organic matter present.

2. Solution of Stannous Chloride.

About 10 gm. of pure tin in thin pieces (or granulated) are put into a large platinum capsule, about 200 c.c. strong pure hydrochloric acid poured over it, and heated till it is dissolved ; or it may be dissolved in a porcelain capsule or glass flask, adding pieces of platinum foil to produce a galvanic current. The solution so obtained is diluted to about a litre with distilled water, and preserved in the bottle (fig. 24) to which the air can only gain access through a strongly alkaline solution of pyrogallic acid. When kept in this manner, the strength will not alter materially in a month. If not so preserved, the solution varies considerably from day to day, and therefore should always be titrated before use if required for quantitative analysis.

IODINE AND SODIUM THIOSULPHATE.

The principle of this now beautiful and exact method of analysis was first discovered by Dupasquier, who used a solution of sulphurous acid instead of sodium thiosulphate. Bunsen improved his method considerably by ascertaining the sources of failure to which it was liable, which consisted in the use of a too concentrated solution of sulphurous acid. The reaction between iodine and very dilute sulphurous acid may be represented by the equation—

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4.$$

If the sulphurous acid is more concentrated, *i.e.*, above 0·04 per cent., in a short time the action is reversed, the irregularity of decomposition varying with the quantity of water present, and the rapidity with which the iodine is added. This irregularity is, however, now obviated by the method of Giles and Shearer in which solutions of SO_2 or sulphites of any strength may be accurately titrated with iodine, by adding the latter to the former in excess, and when the reaction is complete titrating the excess of iodine with thiosulphate.

Sulphurous acid, however, very rapidly changes by keeping even in the most careful manner, and cannot therefore be used for a standard solution. The substitution of sodium thiosulphate is a great advantage, inasmuch as the salt is easily obtained in a pure state, and may be directly weighed for the standard solution. The reaction is as follows :—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6,$$

the result being the formation of sodium iodide and tetrathionate.

In order to ascertain the end of the reaction in analysis by this method an indicator is necessary, and the most delicate and sensitive for the purpose is starch, which produces with the slightest trace of free iodine in cold solution the well-known blue iodide of starch. Hydriodic or mineral acids and iodides have no influence upon the colour. Caustic alkalies destroy it.

The principle of this method, namely, the use of iodine as an indirect oxidizing body by its action upon the elements of water, forming hydriodic acid with the hydrogen and liberating the oxygen in an active state, can be applied to the determination of a great variety of substances with extreme accuracy.

Bodies which take up oxygen, and decolorize the iodine solution, such as sulphurous acid, sulphites, sulphuretted hydrogen, alkali thiosulphates, and arsenites, stannous chloride, etc., are brought into dilute solution, starch added, and the iodine delivered in with constant shaking or stirring until a point occurs at which a final drop of iodine colours the whole blue,—a sign that the substance can take up no more iodine, and that the drop in excess has shown its characteristic effect upon the starch.

Free chlorine, or its active compounds, cannot, however, be titrated with thiosulphate directly, owing to the fact that, instead of tetrathionic acid being produced as with iodine, sulphuric acid is formed, as may be readily seen by testing with barium chloride. In such cases, therefore, the chlorine must be evolved from its compound and passed into an excess of solution of pure potassium iodide, where it at once liberates its equivalent of iodine, which can then, of course, be determined with thiosulphate.

All bodies which contain available oxygen, and which evolve chlorine when boiled with strong hydrochloric acid, such as the chromates, manganates, and all metallic peroxides, can be readily and most accurately determined by this method.

1. Preparation of the Decinormal Solution of Iodine.

12·692 gm. Iodine per litre

Chemically pure iodine may best be obtained by the Stas method. Commercial resublimed iodine is mixed with about one-half of its weight of potassium iodide, and dissolved in half its weight of water, the iodine is then precipitated by water, transferred to a funnel whose neck is filled with freshly ignited asbestos, then well washed to remove the potassium iodide, and dried at a moderate heat, and finally over sulphuric acid. It is then sublimed by gently heating the iodine between two large watch-glasses or porcelain capsules; the lower one being placed upon a heated iron plate, the iodine sublimes in brilliant plates. It is then sublimed again twice, and finally dried over sulphuric acid.

The watch-glass or capsule containing the iodine is placed under the exsiccator to cool, then 12·692 gm. are accurately weighed, and together with about 18 gm. of pure potassium iodide (free from iodate)* dissolved in about 250 c.c. of water and diluted to a litre.

* Morse and Burton (*Amer. Chem. Jour.*, 1888) state that potassium iodide may be completely freed from iodate by boiling a solution of it with zinc amalgam, prepared by shaking zinc dust in good proportion with mercury in presence of tartaric acid and washing with water. The iodate is completely reduced with formation of zinc hydroxide. The pure solution of iodide is filtered for use through a paper filter saturated with hot water.

The flask must not be heated in order to promote solution lest iodine vapours be lost in the operation.

The iodine solution is best preserved in small stoppered bottles, which should be completely filled, and kept in a cool and dark place. It should be used with a tap burette, as it makes rubber tubing hard and useless.

The standardization of the iodine solution may be done in many ways, *e.g.* by pure sodium thiosulphate prepared as described below, or a strictly $^N/_{10}$ solution of it, or again pure arsenious acid or its $^N/_{10}$ solution, with the addition of a little sodium bicarbonate. It may be titrated with barium thiosulphate (BaS_2O_3, H_2O) as proposed by Plimpton and Chorley; this latter salt possesses a high molecular weight, 267·5 parts being equivalent to 126·92 of iodine, but being sparingly soluble in water the titration must be carefully done, inasmuch as the crystalline powder has to be gradually decomposed by the iodine, and the end-point may easily be overstepped. A weighed quantity of the finely powdered salt is put into a stoppered bottle with water, and the iodine solution run in from a burette with continuous shaking, until the salt is nearly dissolved ; starch indicator is then added, and the addition of iodine continued with shaking until the liquid assumes a blue colour that does not disappear on agitation.

Pure barium thiosulphate is easily prepared by mixing together a warm solution of 50 gm. of sodium thiosulphate in 300 c.c. of water, and 40 gm. of barium chloride in a like volume of warm water ; after stirring well, the salt soon separates in fine powdery crystals. These are collected in a funnel stopped with glass or cotton wool, repeatedly washed with cold water till all chlorine is removed, then dried at below 30° C. on a glass or porcelain plate until all extraneous moisture is removed ; or the crystals may be treated, after thorough washing with alcohol and ether, as described below for sodium thiosulphate.

2. Decinormal Sodium Thiosulphate.

24·822 gm. per litre.

$Na_2S_2O_3$, $5H_2O = 248·22$.

It is not difficult either to manufacture or procure pure sodium thiosulphate, but there may be uncertainty as to extraneous water held within the crystals. In order to avoid this Meineke* recommends that the otherwise pure crystals be broken to coarse powder, washed first with pure alcohol, then with ether, and lastly dried in a current of dry air at ordinary temperature. The salt so prepared may be weighed directly, dissolved in a litre of distilled water, and then titrated with the iodine solution and starch. It is advisable to preserve the solution in the dark. After a time all solutions of thiosulphate undergo a slight amount of oxidation, and sulphur deposits upon the bottle ; it is therefore always advisable to titrate it previous to use.

* *Chem. Zeit.* 18, 33.

3. Starch Indicator.

One part of clean potato starch, or arrowroot, is first mixed with cold water into a smooth emulsion, then gradually poured into about 150 or 200 times its weight of boiling water, the boiling continued for a few minutes, then allowed to stand and settle thoroughly. The clear solution only is to be used as the indicator, of which a few drops only are necessary. The solution may be preserved for some time by adding to it a few drops of chloroform, and shaking well in a stoppered bottle, but it is preferable to use a fresh solution in all cases.

Lintner's soluble starch acts well as an indicator, as it gives at once a clear solution in boiling water. The colour which is produced with this form of starch is not quite so pure a blue as that given by a freshly made solution of ordinary starch, owing to the presence of some dextrin unavoidably produced in the preparation, but it is no hindrance to the end-point in practice. In iodimetric analyses it is always advisable in titrating the free iodine with thiosulphate or arsenious solution to delay adding the starch until the iodine colour is nearly removed; a much more delicate ending may be obtained and with very little starch.

Methylene Blue Indicator.—Sinnatt* points out that methylene blue forms a convenient indicator in iodimetric titrations in lieu of starch. In dilute solutions, when a solution of methylene blue is added to a solution of iodine in potassium iodide, the formation of an iodo-compound of the colouring matter is accompanied by a colour change from blue to yellowish-green, and finally to a clear yellowish-brown colour. On the completion of the iodine titration the blue colour recurs. With most reducing agents methylene blue is not reduced, but titanous chloride decolorizes it. 1 c.c. of a 0·005 per cent. solution of the indicator to 50 c.c. of liquid gives a convenient depth of colour for titrations.

Extension of the Iodimetric System.

The verification and extension of iodimetric methods have received considerable attention from a great number of chemists, among whom may be mentioned J. Wagner,† who has studied the accuracy of the determination, by means of thiosulphate solutions, of the iodine liberated from acidified potassium iodide solutions when the oxidizing agents employed are potassium or sodium bromate, potassium dichromate, chromate, and iodate. The titrations should be carried out in flasks and not in beakers; a titration with potassium dichromate and iodide required 25·67 c.c. of thiosulphate when carried out in a flask, and three titrations varied by only 0·01 c.c.; a similar titration in a beaker required 25·52 c.c. of thiosulphate, and three titrations varied as much as 0·07 c.c.

With reference to the application of iodimetry to the determination of acids and alkalies Walker and Gillespie‡ have shown that when iodine acts upon a solution of a metallic hydroxide at a temperature high enough to destroy any trace of hypoiodite a perfectly neutral liquid is produced which contains 1 molecule of iodate to 5 of iodide. On adding dilute acid, these two salts interact in the well-known way, liberating 6 atoms of iodine; and by titration with thiosulphate or arsenious acid, the iodine—that is to say, the original hydroxide—may be determined. Similarly, an acid may be neutralized by a known excess of alkali standardized in this way, when determination of the surplus will give the strength

* *Analyst* 1910, 309.

† *Z. a. C.*, 1899, 427-453. ‡ *Z. a. C.*, 1899, 194.

$6\,OH^- + 3I_2 \rightarrow IO_3^- + 5I^- + 3H_2O$

of the acid. The process has been tested on the hydroxides of the alkalies and alkaline earths, on sulphuric and hydrochloric acids; and although the precautions necessary to avoid loss of iodine and carbonation of the liquid perhaps render it somewhat complicated, the reaction proceeds so smoothly that it should be serviceable for the indirect analysis of acids and probably for other suitable compounds. It cannot, however, be employed on alkali-metal carbonates. The method outlined by Phelps* may with advantage be slightly modified. A moderate excess of decinormal iodine is placed in a lightly-covered conical flask, the alkali is added (or, in determining acid, the acid is added, followed by a measured excess of standard alkali), and the whole is boiled till all free iodine is volatilized. The bulk of the liquid in all tests should be uniform and as small as possible, starting with about 100 c.c. and boiling down to about 35 c.c. The vessel is cooled in a stream of water, 10 c.c. of dilute sulphuric or hydrochloric acid added, and the liquid titrated with thiosulphate and starch in the usual way.

L. W. Andrews† states that, as is well known, when potassium iodide is titrated with chlorine water in a neutral solution, the reaction which takes place is expressed by the equation—

$$KI + 3Cl_2 + 3H_2O = KCl + HIO_3 + 5HCl \quad . \quad . \quad . \quad . \quad (1).$$

On the other hand, it may not be so well known that if a large excess of free hydrochloric acid is present during the titration, chloroform or carbon tetrachloride being used as before for an indicator, the reaction will be—

$$KI + Cl_2 = KCl + ICl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In both cases the end of the reaction is shown by the immiscible solvent becoming colourless. If instead of chlorine water we titrate with a solution of *potassium iodate*, the stage at which the reaction stops is likewise dependent upon the concentration of the acid. If this be low, the reaction goes no further than to set the iodine free in accordance with the equation—

$$5KI + KIO_3 + 6HCl = 6KCl + 3I_2 + 3H_2O \quad . \quad . \quad . \quad (3),$$

while if a great excess of hydrochloric acid is present the reaction runs—

$$2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O \quad . \quad . \quad . \quad (4),$$

the immiscible solvent remaining violet in the former case (No. 3), but in the latter becoming colourless, while the supernatant solution turns bright yellow from the iodine chloride. The probable explanation of this behaviour is that iodine chloride, as the salt of a very weak base, undergoes hydrolysis in a neutral or feebly acid solution, with the production of the corresponding hydroxide and acid; thus—

$$ICl + H_2O = IOH + HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

the iodous hydroxide ("hypoiodous acid"), which is formed, undergoing spontaneous conversion into iodic acid, &c., whereas the hydrolysis is prevented by a great excess of hydrochloric acid.

The reaction of equation (1) was used long ago by A. and F. Dupré (*Liebig's Ann. Chim.*, 1855, xciv. 365) for the titration of *iodides*. In order to compare the reactions of the first two equations, 5 c.c. of a decinormal potassium iodide solution were titrated with chlorine water in presence of 5 c.c. of chloroform. After the addition of 75·4 c.c. of the latter the chloroform became colourless. The titration was now repeated with the further addition of respectively 15, 20, and 30 c.c. of strongest hydrochloric acid, and the amounts of chlorine water required were 25·4, 25·2, and 25·25 c.c., the end-reaction being of extraordinary sharpness. Nearly three times as much chlorine was therefore required in the absence of hydrochloric acid as in its presence, as the theory demands. Probably, if the small amount of acid produced by the reaction itself (Equation 1) had been neutralized by the addition of calcium carbonate the theoretical amount of 75·75 c.c. of chlorine solution would have been required. In order to judge the influence of small quantities of acid, the titration was repeated with addition of 1, 2, 5, and 10 c.c. of concentrated hydrochloric acid, when respectively 34·1, 26·9, 26·0, and 25·6 c.c. of chlorine water were required.

* *Analyst*, 1897, 55.

† *Zeit. anorg. Chem.*, 1903, 76, and *J. Am. Chem. Soc.*, **25**, 756.

From these preliminary experiments, it appeared that the hydrolysis of the iodine chloride might be wholly inhibited by addition of a sufficiency of acid, and that a solution of potassium iodate might be successfully substituted for the chlorine water, thus realizing the reaction of Equation 4. 9·7465 gm. of acid potassium iodate were dissolved in water and made up to 1 litre. According to the theory, each c.c. of this solution should be equivalent to 16·6 mgm. of potassium iodide. To 10 c.c. of a solution of pure potassium iodide (20·6 gm. to the litre), 5 c.c. of chloroform, 20 c.c. of water, and 30 c.c. of concentrated hydrochloric acid (sp. gr. 1·21) were added, and the mixture was titrated in a glass-stoppered bottle of 250 c.c. capacity with the iodate solution, shaking briskly, until the chloroform lost its colour, the end-point being exceedingly sharp. 12·45 c.c. of the iodate solution were required. Hence, 0·20634 gm. potassium iodide was found against 0·20600 taken, or 100·17 per cent. In a second experiment, 15 c.c. of the iodide solution, titrated in the same way with 33 c.c. of hydrochloric acid and no additional water, required 18·6 c.c. of the iodate solution, corresponding to 0·30900 gm. found, against 0·30900 gm. taken, or 100·00 per cent. taken.

The process as described can be applied to the titration of *chromates*. For this purpose the chromate is added to an excess of a titrated potassium iodide solution, with 5 c.c. of chloroform and sufficient concentrated hydrochloric acid to be at least half the volume of the entire mixture at the close of the titration. The titration is then carried out precisely as described above. In one experiment of this sort, 36·3 mgm. of potassium pyrochromate were taken, and 36·8 mgm. found.

The following experiment shows the applicability of the process to the titration of *free iodine* :—0·3447 gm. of pure iodine was weighed and placed in the stoppered bottle previously used, with 5 c.c. of a potassium iodide solution containing 20·6 gm. per litre ; 10 c.c. of fuming hydrochloric acid, and 5 c.c. of chloroform were added, and the titration was carried out in the usual way. Required, 19·85 c.c. of standard iodate. Since 6·20 c.c. are required for the iodide, 13·65 c.c. remain as corresponding to the free iodine, or 0·3467 gm. iodine found ; 100·46 per cent.

To determine whether the method can be used for determination of *chlorates*, and under what conditions, the succeeding experiments were tried. Five c.c. of a solution of potassium chlorate containing 70·3 mgm. of the pure salt was added to 25 c.c. of the potassium iodide solution mentioned above, and 50 c.c. of fuming hydrochloric acid. After standing fifteen minutes in the stoppered bottle, 5 c.c. of chloroform were added, and the titration completed. Required, 13·65 c.c. of the iodate. As the iodide is equivalent to 31·0 c.c. 17·35 c.c. correspond to the chlorate, whence 70·9 mgm. of potassium chlorate were found. In a second similar experiment, only 40 c.c. of hydrochloric acid were used, and the mixture was titrated at once, without standing. In this case 14·0 c.c. of iodate were required, hence 69·55 mgm. of chlorate were found. This shows, as was expected, that the chlorate must be left for some time in contact with the hydrochloric acid and potassium iodide for the completion of the reaction. In a third experiment, exactly similar to the last except that the mixture was allowed to stand twenty-four hours before titration, 13·75 c.c. of iodate were required, whence 70·4 mgm. of chlorate were found. It is therefore a matter of indifference whether the time of digestion is a quarter of an hour or twenty-four hours. In a fourth experiment, 5 c.c. of another potassium chlorate solution containing 33·46 mgm. of the pure salt was allowed to stand for ten minutes with 10 c.c. of iodide solution, and 20 c.c. of fuming hydrochloric acid ; then 5 c.c. of chloroform were added, and the titration was performed. Required, 4·25 c.c. of iodate. Calculated for the iodide, 12·40 c.c., whence 33·39 mgm. of chlorate were found. Other experiments, not necessary to detail, show that there must be a decided excess of iodide as compared with the chlorate ; otherwise the results are likely to be a little too low. The necessary working conditions for the titration of a *chlorate* can be prescribed as follows :—

To the solution of the chlorate, add an exactly known amount of pure potassium iodide (a titrated solution may be used), in a glass-stoppered bottle, and an amount of fuming, pure hydrochloric acid at least one-third greater than the

volume of the solution. Close the bottle tightly, and allow it to stand fifteen minutes after shaking, then add 5 c.c. of chloroform. On now shaking, the chloroform must become deep violet. If the colour is pale, an insufficiency of iodide has been added, and it is better to begin again rather than to attempt to bring the analysis into order. Now add the decinormal iodate with intermittent violent shaking until the chloroform becomes colourless, which point can be determined with the utmost precision. Each c.c. of a decinormal iodate solution is equivalent to 2·782 mgm, of (ClO_3).

Solutions of *arsenious acid or chloride* can be titrated in the same way as iodides, the reaction being expressed by the equation—

$$2AsCl_3 + KIO_3 + 5H_2O = 2H_3AsO_4 + KCl + ICl + 4HCl.$$

In this case, however, unlike the other, a too great concentration of hydrochloric acid must be avoided, since under those conditions the end-point becomes obscure, probably a phenomenon connected with the formation and dissociation of arsenic pentachloride. The suitable concentration of the acid is therefore confined within somewhat narrow limits, but not so narrow as to cause any practical difficulty in working. It was found that 30 per cent. of hydrochloric acid, calculated on the weight of the entire liquid at the close of the titration, exceeds the permissible maximum limit, while 25 per cent. does not. On the other hand the minimum limit is in the neighbourhood of 12 to 15 per cent. of acid. For the experiments noted below, a solution of sodium arsenite was employed in which the amount of arsenious oxide had been determined by titration with iodine solution in the ordinary way. Taken, 25 c.c. arsenious solution (243·8 mgm. As_2O_3) and 50 c.c. of fuming hydrochloric acid; required, 24·45 c.c. decinormal = 242·1 mgm. of arsenious oxide. Taken, 5 c.c. arsenious solution, 5 c.c. hydrochloric acid, and 10 c.c. water; required, 4·9 c.c. of iodate = 48·6 mgm.; found, 48·8 mgm. by iodine titration. Taken, 20 c.c. arsenious solution and 40 c.c. hydrochloric acid; required, 19·7 c.c. iodate = 194·9 mgm. arsenious oxide; found, 194·7 mgm. by iodine titration. Taken, 15 c.c. arsenious solution and 30 c.c. hydrochloric acid; required, 14·8 c.c. iodate = 146·4 mgm. arsenious oxide; found, 146·3 mgm. by iodine titration.

To summarize, add to the arsenious solution an amount of fuming hydrochloric acid sufficient to make the hydrochloric acid equal to about 20 per cent. of the entire mixture at the end of the titration, and 5 c.c. of chloroform; then run in from a burette as large a proportion as can be judged of the whole amount of decinormal iodate requisite, shake well, and continue titrating with the iodate until the chloroform is colourless. Each c.c. of the standard solution corresponds to 9·9 mgm. arsenious acid or 7·5 mgm. arsenic.

The determination of *antimony* is precisely like that of arsenic. A solution was prepared of pure re-crystallized antimonyl tartrate, containing 31·251 gm. per litre. Twenty-five c.c. of this were mixed with 30 c.c. hydrochloric acid and 20 c.c. water, and titrated as usual. 23·6 c.c. of the iodate were required, equivalent to 784·6 mgm. tartar emetic found as against 781·3 mgm. taken. In this determination the amount of hydrochloric acid should have been greater by 15 c.c. In the next experiment, 25 c.c. of the antimonious solution with 25 c.c. of hydrochloric acid required 23·50 c.c. of iodate, equivalent to 780·6 mgm. of antimony salt found (781·3 taken). Twenty-five c.c. antimony solution with 35 c.c. fuming hydrochloric acid required 23·55 c.c. of iodate, whence is calculated 781·2 mgm. potassium antimonyl tartrate.

Since copper does not interfere in the least with the application of the method, it is possible, for example, to titrate the *arsenic in Paris green* directly without preliminary separation. Thus, 20 c.c. of a sodium arsenite solution with 20 c.c. of fuming hydrochloric acid required 8.95 c.c. of iodate, the same, plus 1 gm. of copper sulphate, required 9·00 c.c. of iodate. For the analysis of Paris green, 0·5 gm. of the substance is dissolved in 15 c.c. of water and 25 c.c. of fuming hydrochloric acid, and directly titrated with 5 c.c. of chloroform and the decinormal solution of iodate.

Ferrous salts can be titrated in exactly the same way as iodides. Taken, 2·0874 gm. ammonium ferrous sulphate; required, 26·05 c.c. iodate, equivalent to 297·6 mgm. iron found, or 14·26 per cent.; theory, 14.25 per cent. Unlike the titration with potassium permanganate, oxalic acid does not interfere with

this determination. Taken, 2·0843 gm. ammonium ferrous sulphate and 1 gm. oxalic acid; required, 25·95 c.c. iodate, equivalent to 296·3 mgm. iron, or 14·22 per cent. Ferric salts do not interfere with any of these titrations, nor do bromides to any serious extent, if the amount is small. The end-reaction in the titration of ferrous salts is somewhat slow, and, in spite of the satisfactory results of the test analyses, is lacking in the sharpness that distinguishes the other titrations described in this paper. This difficulty appears to be avoided by the addition of a small amount of manganous chloride, but the point requires further examination.

The method which has been described is adapted to the determination of almost all the substances to which Bunsen's process of distillation with potassium iodide and hydrochloric acid is applicable, with at least equal precision, with less expenditure of time and far simpler apparatus. It is furthermore applicable in certain cases in which the Bunsen method is not, as, for example, the titration of *arsenic* or *antimony* in the presence of copper and ferric compounds.

ANALYSIS OF SUBSTANCES BY DISTILLATION WITH HYDROCHLORIC ACID INTO ALKALI IODIDE.

THERE is a great variety of substances containing oxygen, which when boiled with hydrochloric acid yield chlorine, equivalent to

Fig. 38.

the whole or a part only of the oxygen they contain according to circumstances. Upon this fact is based the variety of analyses which may be accomplished by means of iodine and sodium thiosulphate, or arsenite; the chlorine so evolved, however, is not itself determined, but is conveyed by means of a suitable apparatus into a solution of potassium iodide, thereby liberating an equivalent quantity of iodine. This latter body is then determined by thiosulphate; the quantity so found is, therefore, a measure of the oxygen

existing in the original substance, and consequently a measure of the substance itself. Analyses of this class may be made the most exact in the whole range of volumetric analysis, far outstripping any gravimetric process.

The apparatus used for distilling the substances, and conveying the liberated chlorine into the alkali iodide, may possess a variety of forms, the most serviceable, however, being the kinds devised respectively by Bunsen, Fresenius, Mohr, and others, among which one of the best is so constructed as to avoid the use of corks or india-rubber, which are soon destroyed by the corrosive action of iodine and acid (see p. 8, fig. 43).

Fig. 39.

Bunsen's arrangement consists of an inverted retort, into the neck of which the tube from the small distilling flask is passed.

Owing to the great solubility of HCl in the form of gas, the apparatus must be so constructed that when all chlorine is liberated and HCl begins to distil the liquid may not rush back into the flask owing to condensation.

The best preventive of this regurgitation is, however, one suggested by Fresenius, and applicable to each kind of apparatus; namely, the addition of a few pieces of pure magnesite. This substance dissolves but slowly in the hydrochloric acid, and so keeps up a

constant evolution of CO_2, the pressure of which is sufficient to prevent the return of the liquid.

The apparatus contrived by Fresenius is shown in fig. 38, and is exceedingly useful as an absorption apparatus for general purposes.

Mohr's apparatus is shown in fig. 39, and is, on account of its simplicity of construction, very easy to use.

The distilling flask is of about 2 oz. capacity, and is fitted with a cork soaked to saturation in melted paraffin ; through the cork the delivery tube containing one bulb passes, and is again passed through a common cork, fitted loosely in a stout tube about 12 or 13 inches long and 1 inch wide, closed at one end like a test tube. This tube, containing the alkali iodide, is placed in an hydrometer glass, about 12 inches high, and surrounded by cold water ; the delivery tube is drawn out to a fine point, and reaches nearly to the bottom of the condenser. No support or clamp is necessary, as the hydrometer glass keeps everything in position. The substance to be distilled is put into the flask, and covered with strong hydrochloric acid, the magnesite added, the condenser supplied with a sufficient quantity of iodide solution, and the apparatus put together tightly. Either an argand or common spirit lamp, or gas, may be used for heating the flask, but the flame must be manageable, so that the boiling can be regulated at will. In the case of the common spirit lamp it may be held in the hand, and applied or withdrawn according to the necessities of the case ; the argand spirit or gas lamp can, of course, be regulated by the usual arrangements for the purpose. If the iodine liberated by the chlorine evolved should be more than will remain in solution, the cork of the condensing tube must be lifted, and more solution added. When the operation is judged to be at an end, the apparatus is disconnected, and the delivery tube washed out into the iodide solution, which is then emptied into a beaker or flask and preserved for titration, a little fresh iodide solution is put into the condenser, the apparatus again put together, and a second distillation commenced, and continued for a minute or so, to collect every trace of free chlorine present. This second operation is only necessary as a safeguard in case the first should not have been complete.

The solutions are then mixed together and titrated in the manner previously described. In all cases the solution must be cooled before adding the thiosulphate, otherwise sulphuric acid might be formed.

Instead of the large test tube, some operators use a U tube to contain the potassium iodide, having a bulb in each limb, but the latter is not necessary if magnesite is used.

The solution of potassium iodide may conveniently be made of such a strength that $\frac{2}{10}$ eq. or 33·2 gm. are contained in the litre. 1 c.c. will then be sufficient to absorb the quantity of free iodine representing 1 per cent. of oxygen in the substance analyzed, supposing it to be weighed in the metric system. In examining

peroxide of manganese, for instance, 0·4346 gm. would be used, and supposing the percentage of peroxide to be about sixty, 60 c.c. of iodide solution would be sufficient to absorb the chlorine and keep in solution the iodine liberated by the process; it is advisable, however, to have an excess of iodide, and, therefore, in this case, about 70 c.c should be used. A solution of indefinite strength will answer as well, so long as enough is used to absorb all the iodine. It may sometimes happen that not enough iodide is present to keep all the liberated iodine in solution, in which case it will separate out in the solid form; more iodide, however, may be added to dissolve the iodine, and the titration can then be made as usual.

The process of distillation above described may be avoided in many cases. There is a great number of substances which, by mere digestion with hydrochloric acid and potassium iodide at an elevated temperature, undergo decomposition quite as completely as by distillation. For this purpose a strong bottle with a very accurately ground stopper is necessary; and as the ordinary stoppered bottles of commerce are not sufficiently tight, it is better to re-grind the stopper with a little *very fine* emery and water. It must then be tested by tying the stopper tightly down and immersing in hot water; if any bubbles of air find their way through the stopper the bottle is useless. The capacity may vary from 30 to 150 c.c., according to the necessities of the case.

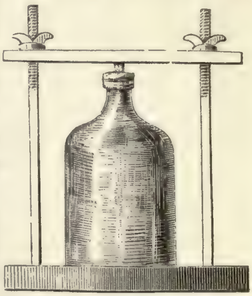


Fig. 40.

The stopper may be secured by fine copper binding-wire, or a kind of clamp contrived by Mohr may be used, as shown in fig. 40; by means of the thumb-screws the pressure upon the stopper may be increased to almost any extent.

The substance to be examined, if in powder, is put into the bottle with pure flint pebbles or small garnets, so as to divide it better, and a sufficient quantity of *saturated* solution of potassium iodide and pure hydrochloric acid added; the stopper is then inserted, fastened down, and the bottle suspended in a water bath, and the water is gradually heated to boiling by a gas flame or hot plate as may be most convenient. When the decomposition is complete the bottle is removed, allowed to cool somewhat, then placed in cold water, and, after being shaken, emptied into a beaker, and the liquid diluted by the washings for titration.

The salts of chloric, iodic, bromic, and chromic acids, together with many other compounds, may be as effectually decomposed by digestion as by distillation, many of them even at ordinary temperatures. Recently precipitated oxides, or the natural oxides when reduced to fine powder, are readily dissolved and decomposed by very weak acid in the presence of potassium iodide (Pickering).

The potassium iodide used in the various analyses must be absolutely free from iodate and free iodine, or, if otherwise, the effect of the impurity must be ascertained by a blank experiment.

ARSENIOUS ACID AND IODINE.

THE principle upon which this method of analysis is based is the fact that when arsenious acid is brought in contact with iodine in the presence of water and free alkali, it is converted into arsenic acid, the reaction being—

$$*\, As_2O_3 + 2I_2 + 2K_2O = As_2O_5 + 4KI.$$

The alkali must be in sufficient quantity to combine with the hydriodic acid set free, and it is necessary that it should exist in the state of bicarbonate, as caustic or monocarbonated alkalies interfere with the colour of the blue iodide of starch used as indicator.

If, therefore, a solution of arsenious acid containing starch is titrated with a solution of iodine in the presence of an alkali bicarbonate, the blue colour does not occur until all the arsenious acid is oxidized into arsenic acid. In like manner, a standard solution of arsenious acid may be used for the determination of iodine or other bodies which possess the power of oxidizing it.

The chief value, however, of this method is found in the determination of free chlorine existing in the so-called chloride of lime, chlorine water, hypochlorites of lime, soda, etc., in solution; generally included under the term of chlorimetry.

Preparation of the $^N/_{10}$ Solution of Alkali Arsenite.

4·948 gm. As_2O_3 per litre.

†$As_2O_3 = 197·92$.

The iodine solution used is the same as described on p. 129.

The corresponding solution of alkali arsenite is prepared by dissolving 4·948 gm. of the purest sublimed arsenious oxide reduced to powder in about 250 c.c. of distilled water in a flask, with about 20 gm. of pure sodium carbonate.‡ See note p. 155.

The mixture needs warming and shaking for some time in order to complete the solution; when this is accomplished the mixture is diluted somewhat, cooled, then made up to the litre.

In order to test this solution, 20 c.c. are put into a beaker with a little starch indicator, and the iodine solution allowed to flow in from a burette, graduated in $\frac{1}{10}$ c.c., until the blue colour appears. If exactly 20 c.c. are required, the solution is strictly decinormal;

* Properly As_4O_6. † Properly As_4O_6.

‡ In a former edition of this book, the arsenious solution was recommended to be made with alkali bicarbonate, but this has, after keeping, been found to give defective results with bleach analyses from some cause not yet understood.

if otherwise, the necessary factor must be found for converting it to that strength.

Iodized Starch-paper.—Starch solution cannot be used for the direct determination of free chlorine, consequently resort must be had to an external indicator; and this is very conveniently found in starch-iodide paper, which is best prepared by mixing a portion of starch solution with a few drops of solution of potassium iodide on a plate, and soaking strips of pure filtering paper therein. The paper so prepared is used in the damp state, and is far more sensitive than when dried.

PART IV.

ANALYSIS BY PRECIPITATION.

THE general principle of this method of determining the quantity of any given substance is alluded to on p. 3, and in all instances is such that the body to be determined forms an insoluble precipitate with a titrated reagent. The end of the reaction is, however, determined in three ways.

1. By adding the reagent until no further precipitate is produced, as in the determination of chlorine by silver.

2. By adding the reagent in the presence of an indicator contained either in the liquid itself, or brought externally in contact with it, so that the slightest excess of the reagent shall produce a characteristic reaction with the indicator; as in the determination of silver with sodium chloride by the aid of potassium chromate, or with thiocyanate and ferric sulphate, or that of phosphoric acid with uranium by the aid of potassium ferrocyanide as indicator.

3. By adding the reagent to a clear solution until a precipitate is formed, as in the determination of cyanogen by silver.

The first of these endings can only be applied with great accuracy to silver and chlorine determinations. Very few precipitates have the peculiar quality of chloride of silver; namely, almost perfect insolubility, and the tendency to curdle closely by shaking, so as to leave the menstruum clear. Some of the most insoluble precipitates, such as barium sulphate and calcium oxalate, are unfortunately excluded from this class, because their finely divided or powdery nature prevents their ready and perfect subsidence.

In all these cases, therefore, it is necessary to find an indicator, which brings them into class 2.

The third class comprises only two processes; viz., the determination of cyanogen by silver, and that of chlorine by mercuric nitrate.

Since the determination of chlorine by precipitation with silver, and that of silver by thiocyanic acid, can be used in many cases for the indirect determination of many other substances with great exactness, the preparation of the necessary standard solutions will now be described.

SILVER AND CHLORINE.

1. Decinormal Solution of Silver.

10·788 gm. Ag or 16·989 gm. $AgNO_3$ per litre.

10·788 gm. of pure silver are dissolved in pure dilute nitric acid with gentle heat in a flask, into the neck of which a small funnel is

dropped to prevent loss of liquid by spirting. When solution is complete, the funnel must be washed inside and out with distilled water into the flask, and the liquid diluted to a litre ; but if it be desired to use chromate as indicator in any analysis, the solution must be neutral. In the latter case the solution of silver in nitric acid is evaporated to dryness, and the residue dissolved in a litre ; or, what is preferable, 16·989 gm. of pure crystallized silver nitrate, previously heated to 120° C. for ten minutes, are dissolved in a litre of distilled water. Fused nitrate of silver is, however, best of all for this purpose. 17·1 grams of the fused salt are dissolved in a litre of distilled water, so as to make a solution rather stronger than is required. A burette is then filled with the solution and it is titrated with 25 c.c. of Decinormal Sodium Chloride Solution in a white porcelain dish, using potassium chromate as indicator. It is then diluted with water to exact strength, and finally tested as before.

2. Decinormal Solution of Sodium Chloride.

5·846 gm. NaCl per litre.

5·846 gm. of pure sodium chloride are dissolved in distilled water, and the solution made up to a litre.

There are two methods by which the analysis may be ended :

(*a*) By adding silver cautiously, and well shaking after each addition till no further precipitate is produced. For details see under Silver 4.

(*b*) By using a few drops of solution of pure potassium chromate as indicator, as devised by Mohr. If the pure salt is not at hand, some drops of silver nitrate solution should be added to the solution of the ordinary salt, to remove chlorine, and the clear liquid used.

The method *b* is exceedingly serviceable, on the score of saving both time and trouble. The solutions must be neutral, and cold. When, therefore, acid is present in any solution to be examined, it should be neutralized with pure sodium or calcium carbonate, or the latter may be added in very slight excess.*

Method of Procedure : To the neutral or faintly alkaline solution two or three drops of a cold saturated solution of chromate are added, and the silver solution delivered from the burette until the last drop or two produce a faint blood-red tinge, an evidence that all the chlorine has combined with the silver, and the slight excess has formed a precipitate of silver chromate ; the reaction is very delicate and easily distinguished. The colour reaction is even more easily seen by gas-light than by daylight. It may be rendered more delicate by adopting the plan suggested by Dupré.† A glass cell, about 1 centimetre in depth, is filled with water tinted with chromate to the same colour as the solution to be titrated. The operation is performed in a white porcelain basin. The faintest appearance of the red change is at once detected on looking through the coloured cell. For the analysis of waters weak in chlorine this method is very serviceable, but, contrary to what has been generally accepted, the accuracy of the results

* Silver chromate is sensibly soluble in the presence of alkali or alkaline earthy nitrates, especially at a high temperature ; sodium and calcium nitrates have the least effect ; ammonium, potassium, and magnesium nitrates the greatest. See also Forbes Carpenter (*J.S.C.I.* **5**, 286).

† *Analyst* **5**, 123.

is seriously interfered with by great dilution or high temperature.* It is, therefore, necessary, as is the case with most volumetric processes in order to secure a high degree of accuracy, to titrate under the same conditions as those observed when the standard was fixed.

INDIRECT DETERMINATION OF AMMONIA, SODA, POTASH, LIME, AND OTHER ALKALIES AND ALKALINE EARTHS, WITH THEIR CARBONATES, NITRATES, AND CHLORATES, ALSO NITROGEN, BY MEANS OF DECINORMAL SILVER SOLUTION AND POTASSIUM CHROMATE AS INDICATOR.

1 c.c. $^{N}/_{10}$ silver solution $= \frac{1}{10000}$ H. eq. of each substance.

MOHR with his characteristic ingenuity has made use of the delicate reaction between chlorine and silver, with potassium chromate as indicator, for the determination of the bodies mentioned above. All compounds capable of being converted into neutral chlorides by evaporation to dryness with hydrochloric acid may be determined with great accuracy. The chlorine in a combined state is, of course, the only substance actually determined ; but as the laws of chemical combination are exact and well known, the measure of chlorine is also the measure of the base with which it is combined.

In most cases it is only necessary to slightly supersaturate the alkali, or its carbonate, with pure hydrochloric acid ; evaporate on the water bath to dryness, and heat for a time to 120° C. in the air bath, then dissolve to a given measure, and take a portion for titration ; too great dilution must be avoided.

Alkalies and Alkaline Earths combined with organic acids are ignited to convert them into carbonates, then treated with hydrochloric acid, and evaporated as before described.

Carbonic Acid in combination may be determined by precipitation with barium chloride, as on p. 96 *et seq.* The washed precipitate is dissolved on the filter with hydrochloric acid (covering it with a watch-glass to prevent loss), and then evaporated to dryness repeatedly till all HCl is driven off. In order to titrate with accuracy by the help of chromate, the baryta must be precipitated by means of a solution of pure sodium or potassium sulphate in slight excess ; the precipitated barium sulphate does not interfere with the delicacy of the reaction. If this precaution were not taken, the yellow barium chromate would mislead.

Free Carbonic Acid is collected by means of ammonia and barium chloride (as on p. 97), and the determination completed as in the case of combined CO_2.

Chlorates are converted into chlorides by ignition before titration.

* W. G. Young, *Analyst* **18**, 125.

Nitrates are evaporated with concentrated hydrochloric acid and the resulting chlorides titrated, as in the previous case.

Nitrogen.—The ammonia evolved from guano, manures, oilcakes, and sundry other substances, when burned with soda lime or obtained by the Kjeldahl method, is conducted into dilute hydrochloric acid; the liquid is carefully evaporated to dryness before titration.

In all cases the operator will, of course, take care that no chlorine from extraneous sources other than the hydrochloric acid is present; or if it exists in the bodies themselves as an impurity, its quantity must be first determined.

EXAMPLE: 0·25 gm. pure sodium carbonate was dissolved in water, and hydrochloric acid added till in excess; it was then dried on the water bath till no further vapours of acid were evolved; the resulting white mass was heated for a few minutes to about 150° C., dissolved and made up to 300 c.c. 100 c.c. required 15·7 c.c $^{N}/_{10}$ silver, this multiplied by 3 gave 47·1 c.c. which multiplied by the $^{N}/_{10}$ factor for sodium carbonate (=0·0053) gave 0·2496 gm. instead of 0·25 gm.

Indirect Determination of Potassium and Sodium existing as Mixed Chlorides.—It is a problem of frequent occurrence to determine the relative quantities of potassium and sodium existing in mixtures of the two chlorides, such as occur, for instance, in urine, manures, soils, waters, etc. The actual separation of potash from soda by means of platinum is tedious, and not always satisfactory.

The following method of calculation is frequently convenient, since a careful determination of the chlorine present in the mixture is the only labour required; and this can most readily be accomplished by $^{N}/_{10}$ silver solution and chromate, as previously described.

(1) The weight of the mixed pure chlorides is accurately found and noted.

(2) The chlorides are then dissolved in water, and very carefully titrated with $^{N}/_{10}$ silver and chromate for the amount of chlorine present, which is also recorded; the calculation is then as follows:—

The weight of chlorine is multiplied by the factor 2·103; from the product so obtained is deducted the weight of the mixed chlorides found in (1). The remainder multiplied by 3·6305 will give the weight of sodium chloride present in the mixture.

The weight of sodium chloride deducted from the total as found in (1) will give the weight of potassium chloride.

Sodium chloride × 0·5303 = Soda (Na_2O).
Potassium chloride × 0·6317 = Potash (K_2O).

The principle of the calculation, which is based on the atomic constitution of the individual chlorides, is explained in most of the standard works on general analysis. Indirect methods like this can only give useful results when the atomic weights of the two substances differ considerably, and when the proportions are approximately equal.

Another method of calculation in the case of mixed potassium and sodium chlorides is as follows:—

The weight of the mixture is first ascertained and noted; the chlorine is then found by titration with $^{N}/_{10}$ silver, and calculated to NaCl; the weight so obtained is deducted from the original weight of the mixture, and the remainder multiplied by 2·42857 will give the potassium.

SILVER AND THIOCYANIC ACID.

THIS excellent and most accurate method has been devised by Volhard* and fully described by the author, and has been favourably noticed by many other well known chemists. It differs from Mohr's chromate method in that the silver solutions may contain free nitric acid, which renders it of great service in indirect analyses.

This method is based on the fact that when solutions of silver and an alkali thiocyanate are mixed in the presence of a ferric salt, so long as silver is in excess the thiocyanate of that metal is precipitated, and any brown ferric thiocyanate which may form is at once decomposed. When, however, the thiocyanate is added in the slightest excess, brown ferric thiocyanate is formed, and asserts its colour even in the presence of much free acid. The method may, of course, be used for the determination of silver, and, by the residual process, for the determination of substances which are completely precipitated by silver. In cases where chlorine is precipitated by excess of silver, and the excess has to be found by thiocyanate, experience has proved that it is absolutely necessary to filter off the chloride and titrate the filtrate and washings. If this be not done the solvent effect of the thiocyanate upon the AgCl will give inaccurate results. This fact seems to have been overlooked at the time the method was first introduced.

It may be used for the determination of silver in the presence of copper up to 70 per cent.; also in presence of antimony, arsenic, iron, zinc, manganese, lead, cadmium, bismuth, and also cobalt and nickel, unless the proportion of these latter metals is such as to interfere by intensity of colour.

It may further be used for the indirect determination of chlorine, bromine, and iodine, in presence of each other, existing either in minerals or inorganic compounds, and for copper, manganese, and zinc; these will be noticed under their respective heads.

1. Decinormal Ammonium or Potassium Thiocyanate.

This solution cannot be prepared by weighing the thiocyanate direct, owing to the deliquescent nature of the salts; therefore about 8 gm. of the ammonium, or 10 gm. of the potassium, salt may be dissolved in about a litre of water as a basis for getting an exact solution, which must be finally adjusted by a correct decinormal silver solution.

The standard solution so prepared remains of the same strength for a very long period if preserved from evaporation.

2. Decinormal Silver Solution.

This is the same as described in a preceding section (p. 141), and may contain free nitric acid if made direct from metallic silver.

* *Liebig's Ann. d. Chem.* **190**, 1.

3. Ferric Indicator.

This may consist simply of a saturated solution of iron alum; or may be made by oxidizing ferrous sulphate with nitric acid, evaporating with excess of sulphuric acid to dissipate nitrous fumes, and dissolving the residue in water so that the strength is about 10 per cent.

5 c.c. of either of these solutions are used for each titration, which must always take place at ordinary temperatures.

4. Pure Nitric Acid.

This must be free from the lower oxides of nitrogen, secured by diluting the usual pure acid with about a fourth part of water, and boiling till perfectly colourless, It should then be preserved in the dark.

The quantity of nitric acid used in the titration may vary within wide limits, and seems to have no effect upon the precision of the method.

EXAMPLE: 50 c.c. of $^N/_{10}$ silver solution are measured into a flask, diluted somewhat with water, and 5 c.c. of ferric indicator added, together with about 10 c.c. of nitric acid. If the iron solution should cause a yellow colour, the nitric acid will remove it. The thiocyanate is then delivered in from a burette; at first a white precipitate is produced rendering the fluid of a milky appearance, and as each drop of thiocyanate falls in, it produces a reddish-brown cloud which quickly disappears on shaking. As the point of saturation approaches, the precipitate becomes flocculent and settles easily; finally, a drop or two of thiocyanate produces a faint brown colour which no longer disappears on shaking. If the solutions are correctly balanced, exactly 50 c.c. of thiocyanate should be required to produce this effect.

The colour is best seen by holding the flask so as to catch the reflected light of a white wall or a suspended sheet of white paper.

Precision in Colour Reactions

DUPRÉ* adopts the following ingenious method for colour titrations:—As is well known, the change from pale yellow to red, in the titration of chlorides by means of silver nitrate with neutral chromate as indicator, is more distinctly perceived by gas-light than by daylight; and in the case of potable waters, containing from one to two grains of chlorine per gallon, it is absolutely necessary to concentrate by evaporation previous to titration, or else to perform the titration by gas or electric light. The adoption of the following simple plan enables the operator to perceive the change of colour as sharply, and with as great a certainty, by daylight as by artificial light. Nevertheless, as has been before mentioned, it is impossible to get accurate results with very weak solutions of chlorine unless the silver solution is standardized upon similar solutions.

The water is measured into a white porcelain dish (100 c.c. are a useful quantity), a moderate amount of neutral chromate is added (sufficient to impart a marked yellow colour to the water), but, instead of looking at the water directly, a flat glass cell containing some of the neutral chromate solution is interposed between the eye and the dish. The effect of this is to neutralize the yellow tint of the water; or, in other words, if the concentration of the solution in the cell is even moderately fairly adjusted to the depth of tint imparted to the water, the

* *Analyst* **5**, 123.

appearance of the latter, looked at through the cell, is the same as if the dish were filled with pure water. If now the standard silver solution is run in, still looking through the cell, the first faint appearance of a red coloration becomes strikingly manifest; and what is more, when once the correct point has been reached the eye is never left in doubt, however long we may be looking at the water. A check experiment in which the water, with just a slight deficiency of silver, or excess of chloride, is used for comparison is therefore unnecessary.

A similar plan will be found useful in other titrations. Thus, in the case of turmeric, the change from yellow to brown is perceived more sharply and with greater certainty when looking through a flat cell containing tincture of turmeric of suitable concentration than with the naked eye. The liquid to be titrated should, as in the former case, be placed in a white porcelain dish. Again, in determining the amount of carbonate of lime in a water by means of decinormal acid and cochineal, the exact point of neutrality can be more sharply fixed by looking through the cell filled with a cochineal solution. In this case the following plan is found to answer best. The water to be tested—about 250 c.c.—is measured into a flat porcelain evaporating dish, part of which is covered over with a white porcelain plate. The water is now tinted with cochineal as usual, and the sulphuric acid run in, the operator looking at the dish through the cell containing the neutral cochineal solution. At first the tint of the water and the tint in which the porcelain plate is seen are widely different; as, however, the carbonate becomes gradually neutralized, the two tints approach each other more and more, and when neutrality is reached they appear identical; assuming that the strength of the cochineal solution in the cell, and the amount of this solution added to the water, have been fairly well matched. Working in this manner it is not difficult (taking ¼ litre of water) to come within 0·1 c.c. of decinormal acid in two successive experiments, and the difference need never exceed 0·2 c.c. In the cell employed the two glass plates are a little less than half an inch apart.

A somewhat similar plan may be found useful in other titrations, or, in fact, in many operations depending on the perception of colour change.

PART V.

APPLICATION OF THE FOREGOING PRINCIPLES OF ANALYSIS TO SPECIAL SUBSTANCES.

ALUMINIUM.

$Al = 27 \cdot 1$.

ALUMINIUM salts (the alums and aluminium sulphates used in dyeing and paper-making) may be titrated for alumina in the absence of iron (except for mere traces) by mixing the acid solutions with a tolerable quantity of sodium acetate, then a known volume in excess of $^{N}/_{10}$ phosphate solution (20·9 gm. of ammonio-sodium phosphate per litre), heating to boiling, without filtration; the excess of phosphate is found at once by titration with standard uranium. If iron in any quantity is present, it may be determined in a separate portion of the substance, and its amount deducted before calculating the alumina. The latter is precipitated as $AlPO_4$, and any iron in like manner as $FePO_4$. Each c.c. of $^{N}/_{10}$ phosphate$=0 \cdot 00513$ gm. Al_2O_3. This method is only available for rough purposes.

Baeyer's Method.—As originally proposed, this process for determining alumina in alums and aluminic sulphates was carried out by two titrations, a measured portion of the solution being first treated with an excess of normal soda sufficient to dissolve the precipitate of hydrate of alumina first formed. It was then diluted to a definite volume, one half being titrated with normal acid and litmus, the other half with tropœolin OO, the difference being calculated to alumina.

A considerable improvement, however, has been made by using phenolphthalein as the indicator, one titration only being necessary. The method is based on the fact that if to a solution of alumina, containing the indicator, normal soda is added in excess, or until the red colour is produced, and normal acid be then added until the colour disappears, the volume of acid so required is less than the soda originally added in proportion to the quantity of alumina present.

The volume of acid which so disappears is in reality the quantity necessary to combine with the alumina set free by the alkali; and

if this deficient measure of acid be multiplied by the factor 0·01716 ($\frac{1}{6}$ mol. wt. of Al_2O_3), the weight of alumina will be obtained. This factor is given on the assumption that the normal sulphate Al_23SO_4, is formed.

The titration must take place in the cold and in dilute solutions. Very fair technical results have been obtained by me with potash and ammonia alums and the commercial sulphates of alumina.

Alumina existing as aluminate of alkali in caustic soda, for instance, may be very well determined by taking advantage of the fact that such alumina is quite indifferent to methyl orange, but reacts acid with phenolphthalein. This fact has been recorded by Thomson and others, but the priority of discovery appears to be due to Baeyer,* who, however, used litmus in the place of phenolphthalein and tropœolin OO instead of methyl orange.

Cross and Bevan† in their examination of caustic soda for alumina found by experiment that the mean of the difference between the titration with methyl orange and that with phenolphthalein required the factor 0·0205 per c.c. of normal acid for the alumina, pointing to the salt as $2Al_2O_3 : 5SO_3$.

The determination of the alumina in caustic soda has given rise to much discussion between even very experienced operators, notably Cross and Bevan and Lunge, but the former chemists have proved, as far as possible by various methods, the accuracy of their views that the above-named equation is correct. The method adopted by them consists in boiling the weighed sample with a slight excess of standard acid, allowing to cool and titrating back with standard soda and phenolphthalein. The acid so consumed represents the total alkali present. To a similar portion a slight excess of acid is added and titrated back with soda and methyl orange.

Determination of free Acid.—Alum cakes or aluminic sulphates of various kinds often contain free H_2SO_4, and many methods have been proposed for its determination. Baeyer titrates a 10 per cent. solution of the substance in water with normal soda and tropœolin OO or methyl orange.

R. Williams‡ adopts the alcohol method, digesting the substance for at least twelve hours with strong alcohol, filtering off and washing with the same, and titrating the solution without dilution or evaporation with $^{N}/_{10}$ acid and phenolphthalein.

Beilstein and Grosset|| have examined with great care all the methods proposed for this purpose, and have devised one which gives very good technical results.

METHOD OF PROCEDURE : 1 to 2 gm. of substance is dissolved in 5 c.c. of water, 5 c.c. of a cold saturated neutral solution of ammonium sulphate added, and stirred for a quarter of an hour. 50 c.c. of 95 per cent. alcohol are then added,

* *Z. a. C.* **24**, 542. † *J. S. C. I.* **8**, 252. ‡ *C. N.* **56**, 194.

|| *Bull. de l'Academie Imp. des Sciences de St. Petersburg*, **13**, 41.

the mixture thrown on a small filter, and washed with 50 c.c. of the same alcohol. The filtrate is evaporated on the water bath, the residue dissolved in water, and titrated with $^N/_{10}$ alkali and litmus. The whole of the neutral aluminic sulphate is precipitated as ammonia alum, the alcohol contains all the free acid.

A. H. White* has proposed another method of determining aluminium sulphates : the summary is as follows :—

If a solution of an alum to which has been added neutral potassium sodium tartrate (Rochelle salt) is titrated with barium hydroxide, the barium hydroxide used will correspond to the sulphuric acid combined with the alumina plus the free acid. The sulphuric acid combined with sodium or potassium is not determined. If a duplicate solution of alum is evaporated to dryness, re-dissolved in neutral sodium citrate, and titrated with barium hydroxide, a smaller quantity of barium hydroxide is required, and the difference between the amounts of barium hydroxide used in the two titrations is equivalent to one-third of the alumina. From these two titrations can be calculated the alumina and the sulphuric acid combined with it, whether the alum be basic or acid, and if the alum is acid the excess of acid over that necessary to form the normal sulphate. Commercial aluminium sulphate may, in its solid state, carry free acid, although in the solution such uncombined acid may disappear, combining with what had been basic portions of the solid salt. Such free acid may be determined by dissolving the solid salt directly in citrate, and titrating with barium hydroxide at once. This method gives results closely concordant with Beilstein and Grosset's method, but it does not show that the alum contains more acid than is sufficient to form with the alumina the normal salt.

Iodimetric Method of A. Stock.†—Reagents required: A mixture of equal parts of a 25 % solution of potassium iodide and a saturated solution of iodate (containing 6-7 % of the salt). Standard sodium thiosulphate (20 % solution).

When a mixture of potassium iodide and iodate is added to a solution of an aluminium salt, a precipitate of aluminium hydrate is formed and a quantity of iodine set free according to the following equation :—

$$Al_2\,(SO_4)_3 + 5\,KI + KIO_3 + 3\,H_2O = 2\,Al(OH)_3 + 3\,K_2SO_4 + 3\,I_2.$$

The reaction, although commencing rapidly in the cold, is not complete for some days, especially in dilute solutions. The rapidity is increased if the liberated iodine be removed by means of standard thiosulphate, especially when warmed. By heating the solution on a water-bath the reaction is complete in a few minutes, even in the case of very dilute solutions. The process is not available in a solution containing tartaric, oxalic, or phosphoric acid, but boric acid does not appear to interfere.

METHOD OF PROCERURE : The solution is first neutralized with sodium hydrate, as it must be neither too acid nor alkaline, then some of the iodide and iodate reagent added. After five minutes the sodium thiosulphate solution is run in from a burette until the solution becomes decolourized, then a further quantity of the iodide reagent added to make sure of complete precipitation. After heating on a water-bath for half an hour, the flocculent precipitate is filtered off and the titration of the filtrate with standard thiosulphate completed.

* *J. Am. C. S.* **24**, 457.

† *Compt. rend.* **130** [4] 175, and *J. S. C. I.*, 1900, **19**, 276.

ANTIMONY.

$Sb = 120 \cdot 2$.

1. Conversion of Antimonious Acid in Alkaline Solution into Antimonic Acid by Iodine (Mohr).

ANTIMONIOUS oxide, or any of its compounds, is brought into solution as tartrate by tartaric acid and water; the excess of acid neutralized by sodium carbonate; then a cold saturated solution of sodium bicarbonate added, in the proportion of 10 c.c. to about 0·1 gm. Sb_2O_3; to the clear solution starch is added and $^N/_{10}$ iodine until the blue colour appears. No delay must occur in the titration when the bicarbonate is added, otherwise a portion of the metal is precipitated as antimonious hydrate, upon which the iodine has little effect. Dunstan and Boole* have proved that the accurate determination of the antimony in tartar emetic may be secured by this method, using the precautions mentioned.

For the determination of *antimonic acid* and its salts, G. von Knorre† gives the following method as accurate :—

METHOD OF PROCEDURE: The solution of the salt, strongly acidified with hydrochloric acid, is treated in a roomy flask with strong solution of sodium sulphite, added gradually in small portions. It is then vigorously boiled until all SO_2 is expelled, a drop of phenolphthalein is added, then caustic potash until red; this is in turn removed by a small excess of tartaric acid. Sodium bicarbonate is then added, and the titration with iodine carried out in the usual way.

The colour disappears after a little time, therefore the first appearance of a reddish tint with starch is accepted as the true measure of iodine required. Greater accuracy is attained by adding an excess of 1 c.c. of $^N/_{100}$ iodine and titrating back with thiosulphate.

$$1 \text{ c.c. } ^N/_{10} \text{ iodine} = 0 \cdot 006 \text{ gm. Sb.}$$

In the case of commercial oxides of antimony, 1 gm. of material is dissolved in 10 c.c. of strong HCl and gaseous H_2S passed through it to remove As. The solution is put into a 250 c.c. flask, the beaker being rinsed with strong HCl and an equal volume of water. All H_2S is removed by a current of air. 5 gm. of tartaric acid are then added, the liquid diluted to the mark with water, and a portion filtered through a dry filter. 25 c.c. are taken and neutralized with sodium bicarbonate, a pinch of the latter together with starch is then added, and the mixture titrated with $^N/_{10}$ iodine.

In the case of sulphides 1·5 gm. is dissolved in hot, strong HCl, and when perfectly cold treated with H_2S, and the titration carried out as before.

Determination of Antimony in presence of Tin (Type and Britannia metal, etc.).‡—The finely divided alloy is dissolved in strong hydrochloric acid by heat, adding frequently small quantities of potassium chlorate. The liquid is boiled to remove free chlorine, cooled, a slight excess of strong solution of potassium iodide added, and the liberated iodine determined by standard thiosulphate.

* *Pharm. Jour., Nov.*, 1888. † *Zeit. angew. Chem.*, 1888, 155

‡ See also H. Yockey, *J. A. C. S.* 1906, 1435.

Mohr's process for the determination of antimonious oxide is both convenient and exact. It depends on the reaction

$$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI.$$

which takes place in a solution containing an excess of alkali bicarbonate. The above equation shows that 120·2 parts of antimony (as Sb_2O_3) are equivalent to 253·84 parts Iodine, and the weight of Iodine found multiplied by 0·4735 = Sb.

Clark* has made experiments as to the value of this process in antimony ores and alloys, and makes the following remarks with respect to them.

Mohr's process leaves nothing to be desired in point of sharpness and accuracy; and the chief object of my experiments has been to ascertain the best condition for the application of this method to the determination of antimony in ores and metals. I have proved by experiments that the presence of lead, even in large quantity, has no influence on the result, but the process is affected by iron, and by copper, arsenic, and tin in the lower state of oxidation. The following is a short summary of my results :—

I. In the case of pure antimony ores practically free from arsenic and iron, the ore may be dissolved in HCl, heated till all the H_2S has been driven off, then mixed with tartaric acid or Rochelle salt, rendered alkaline by bicarbonate of soda, and titrated with $^N/_{10}$ iodine solution, as recommended by Mohr. 1 gm. antimony ore containing traces of Fe gave antimony 46·77 per cent. Another 1 gm. antimony ore containing traces of Fe gave antimony 46·80 per cent.

II. When the ore contains more than traces of iron, it is dissolved in HCl, precipitated with H_2S, filtrated, washed, re-dissolved in HCl, and the antimony titrated in an alkaline tartrate solution as before.

III. When the ore contains arsenic, which is by no means a rare occurrence, it is dissolved in strong HCl containing sufficient ferric chloride to decompose the sulphides, and the arsenic is distilled off; the antimony is then precipitated with H_2S, filtered, washed, re-dissolved in HCl, and titrated with $^N/_{10}$ iodine in an alkaline tartrate solution. The arsenic in the distillate can also be titrated with iodine in presence of excess of bicarbonate of soda.

IV. When an alloy or sulphide contains tin as well as arsenic and antimony, it may be dissolved in HCl and Fe_2Cl_6, the arsenic distilled off as before, and the antimony precipitated with metallic iron (which should be as pure as possible, steel filings answer well.) The precipitated antimony, after being filtered and washed, is then dissolved in HCl with the assistance of a little chlorate of potash, filtered from any insoluble impurity derived from the iron, precipitated with H_2S, filtered, washed, dissolved in HCl, boiled to expel H_2S, and titrated with $^N/_{10}$ iodine in an alkaline tartrate solution.

The antimony ore referred to above, when treated in this way, gave the following results :—

1 gm. gave antimony 46·62 per cent. Another 1 gm. gave antimony 46·68 per cent.

Clark has also discovered a modified iodimetric process which may be used where the original process is inadmissible.

When antimony is dissolved in HCl with the assistance of chlorate of potash, nitric acid, or bromine, the oxidizing agent converts the antimony into the highest state of oxidation, on which account it is necessary to reduce it again to render it suitable for the application of Mohr's process. It has been discovered, however, that when antimony is dissolved in HCl with the assistance of iodine, no reducing agent is required, as iodine in an acid solution does not oxidize antimony beyond Sb_2O_3, so that after boiling off the excess of iodine Mohr's process can be at once applied to the solution.

* *J. S. C. I.* **15**, 255.

This action of iodine is of very great importance, as it simplifies very much the determination of antimony in alloys containing lead and tin, as the tin is oxidized by the iodine to the stannic state, and the lead has no influence on the result. In applying the process, a weighed quantity of the alloy is treated with HCl so long as there is any action, then solid iodine is added in small quantities at a time, and heat applied till complete solution has taken place. The excess of iodine is removed by boiling, and the solution cooled, diluted, and mixed with a little starch. Should the addition of starch produce a blue colour in the acid solution owing to the presence of a trace of free iodine, a very weak solution of sulphite of sodium is added drop by drop till the blue colour disappears. It is then mixed with Rochelle salt, rendered alkaline with sodium carbonate and titrated with $^{N}/_{10}$ iodine in the presence of a considerable excess of sodium bicarbonate.

In this way good results were obtained with white metal and alloys containing large proportions of lead; but if copper is present the result is too low, and the copper should be removed by converting the metals into sulphides, and dissolving out the antimony by caustic soda or potash.

2. Oxidation by Potassium Dichromate or Permanganate (Kessler).

$$5SbCl_3 + 16HCl + 2KMnO_4 = 5SbCl_5 + 2KCl + 2MnCl_2 + 8H_2O.$$

Dichromate or permanganate added to a solution of antimonious chloride, containing not less than $\frac{1}{6}$ of its volume of hydrochloric acid (sp. gr. 1·12), converts it into antimonic chloride.

The reaction is uniform only when the minimum quantity of acid indicated above is present, but it ought not to exceed $\frac{1}{3}$ the volume, and the precautions before given as to the action of hydrochloric acid on permanganate must be taken into account, hence it is preferable to use dichromate.

Kessler* has carefully experimented upon this method and adopts the following processes.

A standard solution of arsenious oxide is prepared containing 5 gm. of the pure oxide, dissolved by the aid of sodium hydrate, neutralized with hydrochloric acid, 100 c.c. concentrated hydrochloric acid added, then diluted with water to 1 litre; each c.c. of this solution contains 0·005 gm. As_2O_3, and represents exactly 0·007283 gm. Sb_2O_3.

Solutions of potassium dichromate and ferrous sulphate, of known strength in relation to each other, are prepared in the usual way; and a freshly prepared solution of potassium ferricyanide is used as indicator.

The relation between the dichromate and arsenious solution is found by measuring 10 c.c. of the latter into a beaker, then 20 c.c. hydrochloric acid of sp. gr. 1·12, and from 80 to 100 c.c. of water (to ensure uniformity of action the volume of HCl must never be less than $\frac{1}{6}$ or more than $\frac{1}{3}$); the dichromate solution is then added in excess, the mixture allowed to react for a few minutes, and the ferrous solution added until the indicator shows the blue colour.

* *Poggend. Annal.* **118**, 17.

To find the exact point more closely, ½ or 1 c.c. dichromate solution may be added and again iron, until the precise ending is obtained.

METHOD OF PROCEDURE: The material, free from organic matter, organic acids, or heavy metals, is dissolved in the proper proportion of HCl, and titrated precisely as just described for the arsenious solution; the strength of the dichromate solution having been found in relation to As_2O_3 the calculation as respects Sb_2O_3 presents no difficulty. Where direct titration is not possible the same course may be adopted as with arsenic; namely, precipitation with H_2S and digestion with mercuric chloride.

In the case of using permanganate it is equally necessary to have the same proportion of HCl present in the mixture, and the standard solution must be added till the rose colour is permanent. The permanganate may be safely used with ¼ the volume of HCl, with the addition of some magnesic sulphate, and as the double tartrate of antimony and potassium can readily be obtained pure, and the organic acid exercises no disturbing effect in the titration, it is a convenient material upon which to standardize the solution.

1 c.c. of a solution containing 5·27 gm. of potassium permanganate per litre = 1% Sb in 1 gm. of substance.

3. Distillation of Antimonious or Antimonic Sulphide with Hydrochloric Acid, and Titration of the evolved Sulphuretted Hydrogen (Schneider).

When either of the sulphides of antimony is heated with hydrochloric acid in Bunsen's, Fresenius', or Mohr's distilling apparatus (p. 135), for every eq. of antimony present as sulphide, 3 eq. of H_2S are liberated. If, therefore, the latter be determined, the quantity of antimony is ascertained.

METHOD OF PROCEDURE: The antimony to be determined is brought into the form of ter- or penta-sulphide (if precipitated from a hydrochloric acid solution, tartaric acid must be previously added to prevent the precipitate being contaminated with chloride), which, together with the filter containing it, is put into the distilling flask with a tolerable quantity of hydrochloric acid not too concentrated. The absorption tube contains a mixture of caustic soda or potash with a definite quantity of $^N/_{10}$ arsenious acid solution in sufficient excess to retain all the sulphuretted hydrogen evolved. The flask is then heated to boiling, and the operation continued till all evolution of sulphuretted hydrogen has ceased; the mixture is then poured into a beaker, and acidified with hydrochloric acid, to precipitate all the arsenious sulphide. The whole is then diluted to, say, 300 c.c., and 100 c.c. taken with a pipette, neutralized with sodium carbonate, some bicarbonate added, and titrated for excess of arsenious acid with $^N/_{10}$ iodine and starch. The separation of antimony may generally be ensured by precipitation as sulphide. If arsenic is precipitated at the same time, it may be removed by treatment with ammonium carbonate.

4. Titration with Standard Potassium Bromate (Györy).*

This method was originally devised for the valuation of Fowler's solution and of tartar emetic, hence it is applicable to both arsenic and antimony.

$$2\ KBrO_3 + 2\ HCl + 3\ Sb_2O_3 = 2KCl + 2\ HBr + 3\ Sb_2O_5.$$

* *Z. a. C.* 1893, 32, 415.

Reagent required:

Decinormal potassium bromate—2·784 gm. of the pure crystals dried at 110° C. are dissolved in water and made up to 1 litre.

1 c.c. $=0·004948$ gm. As_2O_3 0·1157 Bi_2O_3

1 c.c. $=0·00721$ gm. Sb_2O_5.

The titration is performed in a solution acidified with HCl. For a 1 % solution of arsenious acid an equal volume of dilute HCl (1 : 2) is used; but in the case of antimony more acid must be taken in order to prevent the precipitation of the antimony with increasing dilution during titration. Thus, for 0·3 gm. of tartar emetic 25 c.c. or more of the dilute acid should be added. Methyl orange is added to the solution as indicator. In each case the slightest excess of bromate completely decolorizes the red solution in consequence of the liberation of bromine. The bromate solution should be added gradually, especially towards the end. The presence of tin and of considerable quantities of iron and copper interferes with this method.

5. Determination of Antimony Pentoxide and its Compounds (Weller).

This is the converse of method 1. The pentachloride is distilled with strong HCl and KI in one of the forms of distilling apparatus (see figs. 38 and 39), and the separated iodine titrated with N/10 thiosulphate.

NOTE ON THE FOREGOING METHODS: E. Schmidt* especially recommends methods 2 and 4 for technical purposes.

Beckett† finds that the volumetric determination of antimony with iodine gives very concordant results, but these are only correct when the older atomic weight of antimony (Sb = 122) is used. When the atomic weight Sb = 120·2 is taken the results are about 1 per cent. too low.

ARSENIC.

$As = 74·96$. $As_2O_3 = 197·92$. $As_2O_5 = 229·92$.

1. Oxidation by Iodine (Mohr).

THE principle upon which the determination of arsenious oxide by iodine is based is explained on p. 139.

Experience has shown that in the determination of arsenious compounds by the method there described it is necessary to use sodium bicarbonate for rendering the solution alkaline, as in the case of antimony.‡

METHOD OF PROCEDURE: To a neutral aqueous solution, add about 20 c.c. of saturated solution of sodium bicarbonate to every 0·1 gm. or so of As_2O_3, and then titrate with N/10 iodine and starch. When the solution is acid, it may be neutralized with sodium carbonate, then the necessary quantity of bicarbonate added, and the titration completed as before.

PROCEDURE FOR ARSENIC ACID: This is best done by dissolving the acid in water and boiling with potassium iodide in the presence of hydrochloric acid in

* *Chem. Zeit.* 1910, **34**, 453. † *C. N.* 1910, **102**, 101.

‡ Washburn (*J. A. C. S.* 1908, 31, and *Analyst* **33**, 102) has studied Mohr's method. He suggests the use of sodium phosphate instead of bicarbonate.

large excess until all iodine vapours are dissipated. The H_3AsO_4 is completely reduced to H_3AsO_3. The liquid is then cooled, sodium carbonate added to neutrality, then some bicarbonate, and the arsenious acid titrated with iodine in the usual way. Younger* has verified this method and proved that the reduction is complete; he also states that when the boiled solution cools, the liberation of a slight amount of iodine occurs, which may be prevented by using a few c.c. of glycerine. Of course the arsenic acid must contain no nitric acid, nitrates, or similar interfering bodies.

1 c.c. $^N/_{10}$ iodine $= 0{\cdot}004948$ gm. As_2O_3, or $0{\cdot}005748$ gm. As_2O_5.

The Determination of Arsenic in Alkali Arsenates.—It was originally proposed by Mohr to effect this by passing sulphur dioxide through the solution so as to reduce the arsenic to arsenious acid, boiling off the SO_2, and determining the arsenious acid by iodine as just described. This process, however, was not widely adopted, as it was found defective in many instances for the reason that the mere passing of the gas through the liquid did not ensure complete reduction of the acid.

Holthof† and McKay‡ have experimented largely on this method of determining arsenic, and Holthof proved that various forms of arsenic, on being converted into arsenic acid, would bear evaporation to dryness with HCl without loss, and that arsenic sulphide could be oxidized by strong nitric acid, or with HCl and $KClO_3$, to arsenic acid, and reduced to the lower state of oxidation by copious treatment with SO_2, the method being to add 300 or 400 c.c. of strong solution of SO_2, digest on the water bath for two hours, then boil down to one-half, and when cool add sodium bicarbonate, and titrate with iodine.

McKay shortens the method considerably by placing the mixture in a well-stoppered bottle, tying down the stopper, and digesting in boiling water for one hour. At the end of that time the bottle is removed and allowed to cool somewhat, then emptied into a boiling-flask, diluted with about double its volume of water, and boiled down by help of a platinum spiral to one-half. The liquid is cooled, diluted, and either the whole or an aliquot portion titrated with iodine in the usual way.

For quantities of material representing about 0·1 gm. As, 30 c.c. of saturated solution of SO_2 will suffice, and the reduction may therefore be made in a bottle holding 50 or 60 c.c. (fig. 40). The results are satisfactory. In the case of titrating commercial alkali arsenates, which often contain small quantities of arsenious acid, this must be determined first, and the amount deducted from the total obtained after reduction.

A. Williamson‖ has devised the following ready method as being applicable to commercial arsenates, and has made use of the reaction which takes place between arsenic and hydriodic acids in strong acid solution. In these circumstances arsenic acid

* *J. S. C. I.* **9**, 158. † *Z. a. C.* **22**, 378. ‡ *C. N.* **53**, 221–243.

‖ *Journal of the Society of Dyers and Colourists*, May, 1896.

is quantitatively reduced with liberation of iodine. The reaction is

$$As_2O_5 + 4HI = As_2O_3 + 2H_2O + 2I_2.$$

It was found that the reduction is complete only in strongly acid solution, and that if such a solution be diluted the reverse reaction takes place to a certain extent, a portion of the arsenious becoming oxidized to arsenic acid. The iodine may, however, be determined before dilution by means of thiosulphate, and in the absence of other bodies capable of liberating iodine it may be taken as a measure of the arsenic acid. The acid solution may then be neutralized, and the arsenite titrated with iodine. This serves as a check on the thiosulphate titration.

The reduction may be effected either in hydrochloric or sulphuric acid solution, but in either case a considerable excess of acid must be present, otherwise the reduction is incomplete.

As commercial sodium arsenate usually contains some nitrate, experiments were made to ascertain whether the presence of this salt interferes with the accuracy of the thiosulphate titration. A pure solution of arsenate was prepared as before, and 1 gm. of sodium nitrate added. 25 c.c. of this solution were then treated with potassium iodide and hydrochloric acid, and the iodine titrated with thiosulphate as before. The arsenic acid calculated from the thiosulphate consumed was 100·3, instead of 100. It is evident that the presence of nitrate causes little or no liberation of iodine in the cold, but if the arsenate is digested with hydrochloric acid and potassium iodide in a closed bottle immersed in boiling water the iodine liberated is considerably in excess of that corresponding to the arsenic acid. In this case, the quantity of thiosulphate consumed is of no value. The arsenic can, however, be accurately determined by titrating the arsenite after the iodine has been decolorized.

Instead of hydrochloric acid, 15 c.c. of a mixture of sulphuric acid and water, in equal volumes, may be used. Since the addition of sulphuric acid causes the solution to become slightly heated, it is cooled before titrating the iodine. The results are practically the same as with hydrochloric acid.

Not less than 3 gm. potassium iodide should be added, or complete reduction is not immediately effected. The presence of small quantities of nitrate does not interfere with the accuracy of the thiosulphate titration. Complete reduction can be brought about with 2 gm. potassium iodide and 10 c.c. of sulphuric acid, if the solution is heated for five minutes on the steam bath. A portion of the iodine volatilizes, but no arsenic is lost. The iodine is exactly decolorized with thiosulphate, the solution neutralized and titrated with iodine in the ordinary manner.

PROCEDURE WITH COMMERCIAL ARSENATE OF SODA: 10 gm. are dissolved to 1 litre, and the arsenic acid in 25 c.c. determined by one of the methods given above. The thiosulphate titration records only the arsenic previously existing as arsenic acid. The small proportion of As_2O_3 which usually exists is ascertained

by direct titration. When this is calculated to arsenic acid, and added to that found by thiosulphate, the results approximate very closely to those found by titrating the arsenic.

Determination of Arsenic in presence of Tin.—If both these elements are present in the lower state of oxidation, the tin may be oxidized with iodine in strong acid solution, the arsenic being unaffected. Rochelle salt is then added, the solution neutralized, and the arsenite titrated with iodine.

EXAMPLE: 25 c.c. of $^{N}/_{10}$ sodium arsenite were mixed with 25 c.c. of hydrochloric acid, and 3 gm. stannous chloride added. The tin was then exactly oxidized with standard iodine, and the arsenic titrated in the alkaline solution. 24·9 c.c of $^{N}/_{10}$ iodine were required.

If they are present in the highest state of oxidation, the arsenic may be reduced by one of the methods given under the determination of arsenic acid. The stannic salt is not affected.

It is thus possible to determine the arsenic in a mixture of arsenate and stannate of soda. In presence of a considerable quantity of tin, however, the complete reduction of the arsenic acid is not effected quite as readily as when tin is absent. The following method has given good results :—

4 or 5 gm. of the mixture are dissolved in as small a quantity of HCl as possible, an equal weight of tartaric acid is dissolved in the solution, which is then diluted to 250 c.c. (If the tartaric acid is not added a precipitate forms on dilution which contains both tin and arsenic.) 25 c.c. of this solution are then mixed with 3 gm. potassium iodide and 25 c.c. HCl, sp. gr. 1·16, and the solution heated on the steam bath for two or three minutes to ensure the complete reduction of the arsenic acid. The liberated iodine is exactly decolorized with thiosulphate, and the arsenic determined by titration with iodine in the neutralized solution. A mixture of arsenate and stannate in equal quantities and containing a known percentage of arsenic gave 28·57 instead of 28·75 per cent. of arsenic acid.

2. Oxidation by Potassium Dichromate (Kessler).

This method is exactly the same as that fully described on p. 153 for antimony.

The arsenious compound is mixed with $^{N}/_{10}$ dichromate in excess in presence of hydrochloric acid and water, in such proportion that at least $\frac{1}{6}$ of the total volume consists of hydrochloric acid (sp. gr. 1·12).

The excess of dichromate is found by a standard solution of pure iron, or of double iron salt, with potassium ferricyanide as indicator; the quantity of dichromate reduced is, of course, the measure of the quantity of arsenious converted into arsenic acid.

$$1 \text{ c.c. } ^{N}/_{10} \text{ dichromate} = 0{\cdot}004948 \text{ gm. } As_2O_3.$$

In cases where the direct titration of the hydrochloric acid solution cannot be accomplished, the arsenious acid is precipitated with H_2S (with arsenates at 70° C.), the precipitate well washed, the filter and the precipitate placed in a stoppered flask, together with a saturated solution of mercuric chloride in hydrochloric acid of 1·12 sp. gr., and digested at a gentle heat until the precipitate is white, then water added in such proportion that not less than $\frac{1}{6}$ of the volume of liquid consists of concentrated HCl; $^{N}/_{10}$ dichromate is then added, and the titration with standard ferrous solution completed as usual.

3. Indirect Determination by Distilling with Chromic and Hydrochloric Acids (Bunsen).

The principle of this very exact method depends upon the fact that when potassium dichromate is boiled with concentrated hydrochloric acid, chlorine is liberated in the proportion of 3 eq. to 1 eq. of chromic acid.

If, however, arsenious acid is present, but not in excess, the chlorine evolved is not in the proportion mentioned above, but so much less as is necessary to convert the arsenious into arsenic acid.

$$As_2O_3 + 4Cl + 2H_2O = As_2O_5 + 4HCl.$$

Therefore every 4 eq. of chlorine short of the quantity yielded when dichromate and hydrochloric acid are distilled alone represent 1 eq. arsenious acid. The operation is conducted in some form of the apparatus described on p. 135 et seq.

4. By Precipitation as Uranium Arsenate (Bödeker).

METHOD OF PROCEDURE: The arsenic must exist in the state of arsenic acid (As_2O_5), and the process is in all respects the same as for the determination of phosphoric acid, devised by Neubauer, Pincus and myself (*infra*). The strength of the uranium solution may be ascertained and fixed by pure sodium or potassium arsenate, or by means of a weighed quantity of pure arsenious acid converted into arsenic acid by evaporation with strong nitric acid, then neutralized with alkali, and dissolved in acetic acid. The method of titration is precisely the same as with phosphoric acid; the solution of uranium should be titrated upon a weighed amount of arsenical compound, bearing in mind here, as in the case of P_2O_5, that the titration must take place under precisely similar conditions as to quantity of liquid, the amount of sodium acetate and acetic acid added, and the depth of colour obtained by contact of the fluid under titration with the ferrocyanide solution.

Boam*, who has had large experience in the examination of arsenical ores, recommends this method as being rapid and accurate, and carries it out as follows :—

METHOD OF PROCEDURE: 1 to 1·5 gm. of dried and powdered ore is boiled to dryness with 20-25 c.c. of strong nitric acid; when cool about 30 c.c. of 30 % caustic soda solution is added and boiled for a few minutes; then diluted, filtered and made up to 250 c.c. 25 c.c. of the liquid are acidified with a solution containing 10 per cent. of sodium acetate in 50 per cent. acetic acid, and heated nearly to boiling, then titrated with the standard uranium as usual. For this latter, the same authority recommends what he terms a fourth-normal solution of uranium, containing 17·1 gm. uranium acetate, and 15 c.c. glacial acetic acid made up to 2 litres with water, 1 c.c. being equal to 1·25 mgm. As. But if the method has to be considered accurate, this suggestion can scarcely be adopted, since the uranium acetate of commerce is of indefinite hydration; and moreover, to ensure exactitude, it is necessary that the titration should be carried out with the same proportions of saline matters, acetic acid, etc. as existed when originally standardizing the uranium. I, therefore, unhesitatingly recommend that the uranium should be standardized with a known weight of pure arsenic or arsenate in the presence of the same proportions of sodium hydrate and acetate, acetic acid, etc. as will actually be used in the analysis of an ore. The method may be used for all ores which can be attacked by nitric acid. It is also available for

* *C. N.* **61**, 219.

iron pyrites containing tolerable quantities of arsenic; the ferric arsenate being readily decomposed by excess of NaHO, thus allowing the ferric hydrate to be filtered off free from As.

The solution of arsenic acid must, of course, be free from metals liable to give a colour with the indicator and from phosphates. Alkalies, alkaline earths, and zinc are of no consequence, but it is advisable to add nearly the required volume of uranium to the liquid before heating. The arsenic acid must be separated from all bases which would yield compounds insoluble in weak acetic acid.

The AsH_3 evolved from Marsh's apparatus may be passed into fuming HNO_3, evaporated to dryness, the arsenic acid dissolved in water (antimony, if present, is insoluble), then titrated cautiously with uranium in presence of free acetic acid and sodium acetate as above described.

5. By Standard Silver as Arsenate.

This method has been devised by Pierce of the Colorado Smelting Company, and is as follows :—

Method of Procedure: The finely-powdered substance for analysis is mixed in a large porcelain crucible with from six to ten times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate. The mass is then heated with a gradually increasing temperature to fusion for a few minutes, allowed to cool, and the soluble portion extracted by warming with water in the crucible, and filtering from the insoluble residue. The arsenic is in the filtrate as alkali arsenate. The solution is acidified with nitric acid and boiled to expel CO_2 and nitrous fumes. It is then cooled to the ordinary temperature, and almost exactly neutralized as follows :—Place a small piece of litmus paper in the liquid : it should show an acid reaction. Now gradually add strong ammonia till the litmus turns blue, avoiding a great excess.* Again make slightly acid with a drop or two of strong nitric acid ; and then, by means of very dilute ammonia and nitric acid, added drop by drop, bring the solution to such a condition that the litmus paper, after having previously been reddened, will, in the course of half a minute, begin to show signs of alkalinity. The litmus paper may now be removed and washed, and the solution, if tolerably clear, is ready for the addition of silver nitrate. If the neutralization has caused much of a precipitate (alumina, etc.), it is best to filter it off at once, to render the subsequent filtration and washing of the arsenate of silver easier.

A solution of silver nitrate (neutral) is now added in slight excess; and after stirring a moment to partially coagulate the precipitated arsenate, which is of a brick-red colour, the liquid is filtered, and the precipitate washed with cold water. The filtrate is then tested with silver and dilute ammonia, to see that the precipitation is complete.

The object is now to determine the amount of silver in the precipitate, and from this to calculate the arsenic. The arsenate of silver is dissolved on the filter with dilute nitric acid (which leaves undissolved any chloride of silver), and the filtrate titrated, after the addition of ferric sulphate, with thiocyanate (p. 145).

From the formula $3\ Ag_2O.As_2O_5$, 647·2 parts Ag = 149·92 parts As, or Ag : As = 1 : 0·2316.

A modification of the above method is suggested by J. F.

* Canby neutralizes with an emulsion of zinc oxide.

Bennett* in order to avoid some sources of inaccuracy. He found that it was very difficult to obtain neutrality by either of the processes given, and, by avoiding ammonia, phenolphthalein could be used as an indicator.

METHOD OF PROCEDURE: 0·5 gm. of the finely-powdered substance is fused with 3 to 5 gm. of sodium carbonate and potassium nitrate in equal parts, about one-third being used on the top. On cooling, the mass is extracted with boiling water and filtered. The filtrate, which contains the arsenic as alkali arsenate, is strongly acidified with acetic acid, then boiled to expel CO_2, and, after cooling, treated with a few drops of phenolphthalein and sufficient caustic soda to give an alkaline reaction. The purple-red coloration produced by an excess of alkali is then discharged by acetic acid. A slight excess of neutral silver nitrate is then vigorously stirred in, and the whole left to settle, away from direct sunlight; the supernatant liquid is poured off through a filter, and the precipitate washed by decantation with cold water, then thrown on the filter and thoroughly washed. The funnel is then filled with water and 20 c.c. of strong nitric acid, this liquid is run through the filter into the original beaker, the residue washed thoroughly with cold water, and the filtrate made up to about 100 c.c., then titrated with standard thiocyanate.

Owing to the large amount of arsenate of silver formed from a small quantity of arsenic (nearly six times by weight), it is not at all necessary or even desirable to work with large amounts of substance. 0·5 gm. is usually sufficient for the determination of the smallest quantity of arsenic; and where the percentage is high as little as 0·1 gm. may be taken with advantage. The method has been used with very satisfactory results on the sulphide of arsenic obtained in the ordinary course of analysis.

Substances such as molybdic and phosphoric acids, which behave similarly to arsenic under this treatment, interfere, of course, with the method. Antimony, by forming sodium antimoniate, remains practically insoluble and without effect.

6. Determination of Arsenious Sulphide by Iodine.

J. and H. S. Pattinson† have shown that the separation of arsenic as sulphide from many metals, viz., lead, tin, cadmium, antimony, and bismuth, is complete when made in concentrated hydrochloric acid (sp. gr. 1·16-1·17). The subsequent determination is carried out by the authors as follows:—

METHOD OF PROCEDURE: The precipitate is collected on asbestos in a Gooch crucible and washed with cold water until free from hydrochloric acid. The asbestos felt with the adhering precipitate is then placed in a small beaker; the crucible is wiped out with a little clean ignited asbestos, which is also put into the beaker. 10 or 15 c.c. of concentrated sulphuric acid (specific gravity about 1·83), free from arsenic, are then poured into the beaker, which is then placed without a cover on a hot plate or on a wire gauze over a small Bunsen flame in a good draught closet. As soon as the acid reaches the temperature at which it begins to fume, the arsenious sulphide becomes rapidly decomposed; at first both sulphuretted hydrogen and sulphurous acid are given off (if a cover be put on the beaker the mutual decomposition of these two gases causes a deposition of sulphur on the sides of the beaker). The evolution of sulphuretted hydrogen is over in a few seconds, but the sulphur dioxide takes longer to expel,

* *J. Am. C. S.* **21**, 431. † *J. S. C. I.*, 1898, p. 211.

depending upon the quantity of arsenious sulphide and of free sulphur that may have been mixed with the precipitate. As soon as the decomposition of the arsenious sulphide begins, the liquid becomes darkened in colour, and the heating, which may be brought to and kept at the verge of ebullition of the acid, is continued until this dark colour passes away, when it will be found that all the sulphurous acid has been expelled. It is of the utmost importance that all sulphurous acid should be eliminated at this stage. This takes about 10 to 20 minutes with precipitates of sulphide weighing about 0·02 gm. and nearly free from free sulphur. Arsenious acid remains in solution in the sulphuric acid, and the amount is determined by cooling the acid, diluting with water, nearly neutralizing the acid with concentrated sodium hydrate solution, and then completing the neutralization and rendering alkaline with an excess of sodium bicarbonate, and finally titrating with standard iodine solution and starch. The iodine solution must be standardized against an approximately equal quantity of arsenious acid, to which the same amount of sulphuric acid has been added as was used for the decomposition of the arsenious sulphide precipitate. As sulphuric acid alone usually requires a few tenths of a cubic centimetre of centinormal iodine solution to be added to it before the blue colour of iodide of starch forms, a blank experiment with the stock of acid in use should be made once for all. It was found the best plan to avoid breaking up the asbestos felt, and if possible to put it in the beaker so that the side on which the precipitate lies is on the bottom of the beaker. This prevents the precipitate from becoming detached from the felt and floating to the top of the acid or creeping up the side of the beaker.

This method was used for six months in the course of daily work, alongside of determinations made by weighing the sulphide precipitate, or, after having separated the arsenic by Fischer's distillation process, by titrating the distillate (previously rendered alkaline) with iodine solution, and the results were very concordant.

Experiments show that there is no loss of arsenious acid by volatilization when arsenious sulphide is decomposed by heating with strong sulphuric acid in the manner described.

Determination of Arsenic in Iron Ores, Steel, and Pig Iron (J. E. Stead).—The best method of separating arsenic from iron solutions is undoubtedly that of distilling with hydrochloric acid and ferrous chloride.

Stead found, after many trials and experiments, that if the distillation is conducted in a special manner the whole of the arsenic may be obtained in the distillate, unaccompanied with any traces of ferrous chloride, and that if the hydrochloric acid is nearly neutralized with ammonia, and finally completely neutralized with sodium bicarbonate, the arsenic can be determined with iodine in the usual manner.

The standard solutions required are :—

Arsenious oxide. 0·66 gm. (=0·5 gm. elemental arsenic) of pure arsenious oxide in fine powder is weighed and placed in a flask, with 2 gm. of sodium carbonate and 100 c.c. of boiling distilled water, and the liquid boiled till all the arsenious oxide has dissolved. When cool, 2 gm. of sodium bicarbonate are added and diluted to one litre. 1 c.c. = 0·0005 gm. As.

Iodine solution. 1·7 gm. of pure iodine is dissolved in 2 gm. of potassium iodide and water, the solution diluted to one litre,

then standardized by titrating 20 c.c. of the arsenious solution. If the iodine has been pure, 20 c.c. of the solution should be required just to produce a permanent blue with starch.

These solutions keep fairly well without alteration for several months. It is advisable, however, to ascertain periodically the value of the iodine by titrating it with the arsenic solution.

METHOD OF PROCEDURE FOR STEEL: From 1 to 50 gm. of the steel in drillings are introduced into a 30-ounce flask, and a sufficient quantity of equal parts of strong hydrochloric acid and water is added to dissolve it. The mouth of the flask is closed with a rubber stopper carrying a safety tube and a tube to convey the gas evolved into the Winkler's spiral absorption tubes, containing a strong saturated solution of bromine in water.

The tube is filled to one-third of its length with the solution, and about ½ c.c. of free bromine is run in to replace the bromine which is consumed or carried out with the passing gas.

The contents of the flask are now gently heated to such a degree that a steady but not rapid current of gas passes through the bromine solution.

In about one hour the whole of the steel will be dissolved, and when no more evolution of hydrogen can be observed, the liquid in the flask is well boiled, so as to completely drive all the gas into and through the bromine solution.

The absorption tube is now disconnected, and the bromine solution containing that part of the arsenic which has passed off as gas is rinsed out into a small 100 c.c. beaker, and the excess of bromine is gently boiled off, and the clear colourless solution is poured into the flask. About 0·5 gm. of zinc sulphide is now dropped into the iron solution and the contents are violently shaken for about three minutes, by which time the whole of the arsenic will be in the insoluble state, partly as sulphide and partly as a black precipitate of possibly free arsenic and arsenide of iron.

It has been found that violent agitation for a few minutes is quite as efficacious in effecting the complete separation of arsenic sulphide as the method of passing a current of CO_2 through the solution to remove the excess of hydric sulphide, or allowing it to stand ten or twenty hours to settle out.

The insoluble precipitate is now rapidly filtered through a smooth filter-paper, and the flask is rinsed with cold distilled water. The precipitate usually does not adhere to the filter, and in such cases the paper is spread out flat upon a porcelain slab, and the arsenic compounds are rinsed off with a fine jet of hot water into a small beaker. The precipitate is now dissolved in bromine water, and a drop or two of HCl.

The bromine solution now containing all the arsenic is gently boiled to expel the bromine, and it is then poured into a 10-ounce retort and is distilled with ferrous chloride and hydrochloric acid.

The apparatus used consists of an ordinary Liebig's condenser, but the retort has its neck bent to an angle of about 150°, and this is attached to the condenser, so that any iron mechanically carried over may run back. By this device, the distillate will never contain more than the very slightest trace of iron.

The solution containing the arsenic having been run into the retort, the beaker is washed out and the washings are also poured in. If the solution is much above 20 c.c. in bulk, it is advisable to add a strong solution of ferrous chloride containing about 0·5 gm. of iron in the ferrous state, and for this purpose nothing answers so well as a portion of the steel solution remaining after separating the arsenic, which is first well boiled to free it from hydric sulphide, and should contain about 10 per cent. of soluble iron as ferrous chloride. 5 c.c. of this solution will contain the necessary amount of iron to add to the retort. After adding the chloride, it is best to boil down the solution to about 20 c.c. before adding any HCl, taking care, of course, to collect what liquid distils over. When the necessary concentration has been effected, 20 c.c. of strong HCl are run in, and the distillation is continued till all excepting about 10 c.c. has passed over. A further quantity of 20 c.c. mixed with 5 c.c. of water is run in, and

this is all distilled over. At this point, as a rule, all the arsenic will have passed into the distillate, but it is advisable to make quite certain, and to add a third portion of acid and water, and to distil it over. If the distillation has not been forced, the distillate will be quite colourless. The arsenic in the distillate will exist as arsenious chloride, accompanied with a large excess of hydrochloric acid. A drop of litmus is put into this solution, and strong ammonia is run in until alkaline. It is now made slightly acid with a few drops of HCl, and a slight excess of solid bicarbonate of soda is dropped in. The contents of the flask are now cooled by a stream of water, and, after adding a clear solution of starch, the standard iodine is run in from a burette till a deep permanent blue colouration is produced.

If the steel or iron contains much arsenic, a smaller quantity, say, 1 or 2 gm., may be dissolved in nitric acid of 1·20 specific gravity and the solution evaporated to dryness, the residue being dissolved in hydrochloric acid, and the solution transferred to the retort, and distilled directly with ferrous chloride and hydrochloric acid, care being taken that the distillation is not forced, as as to avoid any of the iron solution passing over into the distillate.

Method of Procedure for Pig Iron: In testing pig irons, they may be dissolved in nitric acid and evaporated to dryness, or be treated in a flask with HCl exactly in the manner described above; but it is advisable, if the latter method is adopted, after treating the voluminous mass of silica and graphite, etc., with bromine and hydrochloric acid, to filter off the insoluble matter and distil the clear solution.

Method of Procedure for Iron Ores: In testing ores, it is only necessary to place the powdered ore directly into the retort, and distil at once with HCl and ferrous chloride, taking care to place a few small pieces of firebrick also in the vessel, to avoid bumping.

If the ore contains much manganese, it is advisable to dissolve it in a separate vessel to liberate and expel the chlorine, and then to transfer it into the retort.

The time taken to test iron or steel need not exceed two hours, and for iron or other ores not much more than half an hour.

It is quite possible accurately to determine as small a quantity as 0·002 per cent. of arsenic by this method.

When dissolving steels in dilute HCl, if there is no rust on the sample or ferric chloride present in the acid, and the presence of air is carefully avoided, as a rule only about one-tenth of the total arsenic present passes off with the gas.

A very simple and accurate method of determining a small amount of arsenic when it exists in the form of freshly precipitated sulphide is suggested by F. Platten.* It consists in simply boiling the sulphide with pure water for a period of from 1 to 3 hours, or until the liquid is quite colourless, and all the H_2S dissipated. The arsenic will then exist wholly as As_2O_3, and may be titrated direct with $^N/_{100}$ iodine, and a slight amount of sodium bicarbonate as usual.

Both this and Stead's method have been proved to give identical results, when carried out by separate skilled operators on the same samples of material.†

7. Titration by Potassium Bromate (Györy).

See under Antimony, p. 154.

* *J. S. C. I.* **13**, 324.

† See also A. H. Low, "Determination of Antimony and Arsenic in Ores," *J. A. C. S* 1906, 1715; and Norton and Koch, "Determination of Arsenic and Antimony in the presence of Organic Matter," *J. A. C. S.* 1905, 1247.

8. Titration by Potassium Iodate (Andrews).

See p. 134 (Applicable to Antimony).

9. Determination of Arsenic in Organic Compounds.

Little, Cahen, and Morgan,* find the most satisfactory process to be a combination of Pringsheim's† method of oxidation by sodium peroxide and Gooch and Browning's volumetric method.‡

METHOD OF PROCEDURE:—0·2-0·3 gm. of the finely-powdered substance is mixed in a nickel crucible with 10-15 gm. of sodium carbonate and sodium peroxide in equal proportions, a portion of these reagents being spread over the mixture. After heating gently for about 15 minutes, the fusion is completed by heating to dull redness for 5 minutes. The contents of the crucible are extracted with water and rinsed into a 450 c.c. conical flask, treated with 25-31 c.c. of sulphuric acid (1 : 1), and the volume reduced to 100 c.c. by boiling. One gm. of potassium iodide is now added and the liquid further concentrated to 40 c.c. After removing the last traces of iodine by means of a few drops of dilute sulphurous acid, the green solution is diluted with hot water and saturated with hydrogen sulphide. The arsenious sulphide is collected, washed, dissolved in 20 c.c. of $^{N}/_{2}$ sodium hydroxide and treated with 30 c.c. of hydrogen peroxide (20 vols.), the excess of the latter being destroyed by heating. A few drops of phenolphthalein are now added, followed by 11 c.c. of sulphuric acid (1 : 1) and 1 gm. of potassium iodide. The solution is concentrated to 40 c.c., decolorised with a few drops of dilute sulphurous acid, diluted with cold water, neutralized with 2N-sodium hydroxide, and slightly acidulated with sulphuric acid. An 11 per cent. solution of sodium phosphate (compare Washburn, *J. Amer. Chem. Soc.*, 1908, **30**, 31), is then added, and the arsenite solution titrated with iodine and starch in the usual way. The volume of sodium phosphate solution added should be about equal to that of $^{N}/_{10}$ iodine required in the titration. Compounds containing little or no oxygen require a proportionately larger quantity of sodium peroxide for oxidation. When the arsenic compound contains iodine, sodium iodate is formed on oxidation, and sufficient sulphurous acid must be added to the acidified extract to reduce this salt to iodide.

BARIUM.

Ba = 137·37.

IN a great number of instances the determination of barium is simply the converse of the process for sulphuric acid (*q. v.*), using either a standard solution of sulphuric acid or a neutral sulphate in a known excess, and finding the amount by residual titration.

When barium can be separated as carbonate, the determination is made as on p. 72.

Precipitation as Barium Chromate.—A decinormal solution of dichromate for precipitation purposes must differ from that used

* *J. Chem. S.* 1909, **95**, 1477. † *Am. Chem. J.* 1904, **31**, 383.
‡ *Am. J. Sci.* 1890, (3), **11**, 66. See also p. 226.

for oxidation purposes. In the present case the solution is made by dissolving 7·37 gm. of pure potassium dichromate in water, and diluting to 1 litre.

METHOD OF PROCEDURE: The barium compound, which may contain alkalies, magnesia, strontia, and lime, is dissolved in a good quantity of water, ammonia free from carbonate added, heated to 60° or 70° C., and the standard dichromate added cautiously, with shaking, so long as the yellow precipitate of barium chromate is formed, and until the clear supernatant liquid possesses a faint yellow colour. 1 c.c. $^N/_{10}$ solution =0·00687 gm. Ba.

Titration of the Precipitate with Permanganate.—In this case the precipitate of barium chromate is well washed, transferred to a flask, and mixed with an excess of ferrous ammonium sulphate; the amount of iron oxidized by the chromic acid is then determined by titration with permanganate; the quantity of iron changed to the ferric state multiplied by the factor 0·8187 = Ba.

Or the barium chromate may be digested with HCl and KI, as described on p. 138. 1 c.c. $^N/_{10}$ thiosulphate = ·004579 gm. Ba.

BISMUTH.

Bi = 208.

THE determination of this metal or its compounds volumetrically has occupied the attention of Pattison Muir, to whom we are indebted for several methods of gaining this end. Two of the best are given here, namely, (1) precipitation of the metal as basic oxalate, and titration with permanganate; (2) precipitation as phosphate with excess of standard sodium phosphate, and titration of that excess by standard uranium acetate.

1. Titration as Oxalate.

Normal bismuth oxalate, produced by adding excess of oxalic acid to a nitric acid solution of the metal, when separated by filtration, and boiled with successive quantities of water three or four times, is transformed into basic oxalate.

METHOD OF PROCEDURE: The solution containing bismuth must be free from hydrochloric acid, as the basic oxalate is readily soluble in that acid. A large excess of nitric acid must also be avoided. Oxalic acid must be added in considerable excess. If the precipitate be thoroughly shaken up with the liquid and the vessel is then set aside, the precipitate quickly settles, and the supernatant liquid may be poured off through a filter in a very short time. If the precipitate be boiled for five or ten minutes with successive quantities of about 50 c.c. of water, it is quickly transformed into the basic salt. So soon as the supernatant liquid ceases to show an acid reaction, the transformation is complete. It is well to employ a solution of permanganate so dilute that at least 50 c.c. are required for the titration ($^N/_{10}$ strength suffices). The basic oxalate may be dissolved in dilute sulphuric acid in place of hydrochloric; it is more soluble, however, in the latter acid. If the solution contains but little hydrochloric acid, there is no danger of chlorine being evolved during the process of titration.

In applying this process to the determination of bismuth in a solution containing other metals, it is necessary, if the solution contain substances capable of acting upon, or of being acted on by, permanganate, to separate the bismuth from the other metals present. This is easily done by precipitating in a partially

neutralized solution with much warm water and a little ammonium chloride. The precipitate must be dissolved in nitric acid, and the liquid boiled down once or twice with addition of the same acid in order to expel all hydrochloric acid, before precipitating as oxalate. The liquid should contain just sufficient nitric acid to prevent precipitation of the basic nitrate before oxalic acid is added, 1 molecule oxalic acid (126·06) corresponds to 1 atom bismuth (208).

1 c.c. $^{N}/_{10}$ permanganate = ·0104 gm. Bi.

A shorter method, based on the same reactions, has been arranged by Muir and Robbs.* In this case, however, the double oxalate of potassium and bismuth is the compound obtained, the excess of oxalate of potash being determined residually. Reis† has shown that when normal potassium oxalate is added to a solution of bismuth nearly free from mineral acid, but containing acetic acid, a double salt of the formula $Bi_2\ (C_2O_4)_3,\ K_2C_2O_4$ is precipitated. In applying this process for the determination of bismuth in mixtures, it is necessary to separate the metal as oxychloride, and that it should be obtained in solution as nitrate with a small excess of nitric acid. This is done by evaporating off the greater part of the free acid, allowing just sufficient to remain that the bismuth may remain in solution while hot. A large excess of acetic acid is then added, it is made up to a definite measure, and an aliquot portion taken for titration.

The solution of normal potassium oxalate standardized by permanganate must not be added in great excess. It is well, therefore, to deliver it into the bismuth liquid from a burette until the precipitation is apparently complete, then add a few extra c.c., and allow to remain for some time with shaking. It is then filtered through a dry filter, a measured portion taken, and the residual oxalic acid found by permanganate.

For determining bismuth in ores the following method has been worked out by Warwick and Kyle.‡

One gm. of the finely powdered ore is evaporated to dryness with 5 or 10 c.c. of strong nitric acid; another 5 c.c. of acid and 25 c.c. of water are added, and the whole is diluted to 100 c.c. Five gm. of ammonium oxalate or oxalic acid are introduced, boiled for five minutes, allowed to settle, and the supernatant liquid filtered off. The precipitate is boiled twice with 50 c.c. of water, and the washings are passed through the same paper. With an ordinary ten per cent. ore this treatment should suffice to convert the bismuth oxalate into the basic salt; but if the filtrate is still acid, boiling must be repeated to neutrality. The precipitate on the paper is then dissolved in 2 to 5 c.c. of 1 : 1 HCl, receiving the liquid in the beaker containing the bulk of the basic oxalate; this is warmed till entirely dissolved, and then diluted to 250 c.c. with hot water. The solution is neutralized with ammonia, and the resulting precipitate taken up in 1 : 4 H_2SO_4, adding a few c.c. in excess. Finally the liquid is titrated at between 70° and 100° C. with permanganate. A permanganate solution in which 1 c.c. = 0·010 gm. Fe will be equal to 0·0186 gm. bismuth; by diluting 100 c.c. of this with 86 c.c. of water a solution of permanganate will be obtained, of which 1 c.c. should equal 0·010 gm. of bismuth. A permanganate solution 1 c.c. = 0·010 gm. Fe; found = 0·01868 gm. Bi. 100 c.c. permanganate above + 86 c.c. of water; 1 c.c. found = 0·01017 gm. Bi. Lead, iron, copper, zinc, arsenic, and tellurium

* *J. C. S.* **41**, 1. † *Berichte*, **14**, 1172. ‡ *C. N.* **75**, 3.

do not interfere with the process. Care must be taken to avoid using too little or too much nitric acid. Hydrochloric acid must not be used to dissolve the ore. The results are accurate enough for all commercial work, and an analysis occupies little time. The figures quoted show maximum errors of -0.0032 and $+0.001$ gm. in determining 0·5 gm. of bismuth in presence of lead, copper, zinc, iron, and arsenic.

2. Precipitation as Phosphate.

The necessary standard solutions are—

(*a*) Standard sodium phosphate containing 35·8 gm. per litre. 1 c.c. $=0.0071$ gm. P_2O_5 or 0·0208 gm. Bi.

(*b*) Standard uranium acetate, corresponding volume for volume with the above, when titrated in the presence of an approximately equal amount of sodium acetate and free acetic acid.

Success depends very much upon identity of conditions, as is explained under Phosphates.

METHOD OF PROCEDURE: The bismuth to be determined must be dissolved in nitric acid; bases other than the alkalies and alkaline earths must be absent. The absence of those acids which interfere with the determination of phosphoric acid by the uranium process (non-volatile, and reducing organic acids, sulphuretted hydrogen, hydriodic acid, etc.) must be assured. As bismuth is readily separated from other metals, with the exception of antimony and tin, by additions of much warm water and a little ammonium chloride to feebly acid solutions, a separation of the bismuth from those other metals which are present should precede the process of estimation. If alkalies or alkaline earths be alone present, the separation may be dispensed with. The precipitated bismuth salt is to be washed, dissolved in a little strong nitric acid, and the solution boiled down twice with addition of a little more nitric acid, in order to remove the whole of the hydrochloric acid present.

Such a quantity of a tolerably concentrated solution of sodium acetate is added as shall ensure the neutralization of the nitric acid, and therefore the presence in the liquid of free acetic acid. If a precipitate form, a further addition of acetate must be made. The liquid is heated to boiling; a measured volume of the sodium phosphate solution is run in; the boiling is continued for a few minutes; the liquid is passed through a ribbed filter, the precipitate being washed repeatedly with hot water; and the excess of phosphoric acid is determined in the filtrate by titration with uranium. If the filtered liquid be received in a measuring flask, which is subsequently filled to the mark with water, and if the inverted uranium method be then employed, the results are exceedingly accurate. This method is especially to be recommended in the determination of somewhat large quantities of bismuth, since it is possible that in such cases a large amount of sodium acetate will have been used, which, as is well known, has a considerably disturbing effect on the reaction of the indicator.

If the bismuth solution contain a large excess of nitric acid, it is better to neutralize nearly with sodium carbonate before adding sodium acetate and titrating.

Fuller details of both the above processes are contained in *J. C. S.* 1877 (p. 674) and 1878 (p. 70).

BROMINE.

Br = 79·92.

THIS element, or its unoxidized compounds, can be determined precisely in the same way as chlorine by $^{N}/_{10}$ silver solution (p. 141),

or by thiocyanate (p. 145), but these methods are seldom of any avail, since the absence of chlorine or its combinations is a necessary condition of accuracy.

Bromine in aqueous solution, or as gas, may be determined by absorption with solution of potassium iodide, in many cases by mere digestion, and in other cases by distillation, in any of the forms of apparatus given on p. 135 et seq., and the operation is carried out precisely as for chlorine (p. 176). 1 eq. I = 1 eq. Br. or I found $\times 0{\cdot}6297 =$ Br.

A process for the determination of bromine in presence of chlorine is still much wanted in the case of examining kelp liquors, etc. Heine* uses a colour method in which the bromine is liberated by free chlorine, absorbed by ether, and the colour compared with an ethereal solution of bromine of known strength. Fehling states that with care the process gives fairly accurate results. It is, of course, necessary to have an approximate knowledge of the amount of bromine present in any given solution.

Reimann† adopts the following method, which gives tolerably accurate results, but requires skill and practice.

The neutral bromine solution is placed in a stoppered vessel, together with a globule of chloroform about the size of a hazel nut. Chlorine water of known strength is then added cautiously from a burette, protected from bright light, in such a way as to ensure first the liberation of the bromine, which colours the chloroform orange yellow; then more chlorine water is added, until the yellowish white colour of chloride of bromine appears ($KBr + Cl_2 = KCl + BrCl$).

The operation may be assisted by making a weak solution of potassium chromate, of the same colour as a solution of chloride of bromine in chloroform, to serve as a standard of comparison.

The strength of the chlorine water is ascertained by potassium iodide and $^N/_{10}$ thiosulphate. 2 eq. Cl = 1 eq. Br.

In examining mother-liquors containing organic matter, they must be evaporated to dryness in presence of free alkali, ignited, extracted with water; then neutralized with hydrochloric acid before titrating as above.

Cavazzi‡ gives a method which answers well for determining bromine in small quantity, when mixed with large proportions of alkali chlorides. It is based on the fact that, when such a mixture is heated to 100° C. with barium peroxide and sulphuric acid, the whole of the bromine is liberated with a mere trace of chlorine; the bromine so evolved is absorbed in any convenient apparatus, such as fig. 38.

The distillation is carried out in a 350 c.c. flask with double-bored stopper; one bore carries an open tube reaching to the bottom of the flask, the other the delivery tube which is connected with the U tubes. The first U tube is empty; the second contains 20 c.c. of a standard solution of arsenious acid in hydrochloric acid, containing 0·005 gm. As_2O_3 in each c.c., and is connected with an aspirator or water pump. The apparatus is arranged so that the flask and empty U tube are immersed in boiling water, the vapours of H_2O_2 are thus decomposed, and the stream regulated by the aspirator.

* *Journ. f. pract. Chem.* **36**, 184. † *Annal. d. Chem. u. Pharm.* **115**, 140.

‡ *Gazz. Chim. Ital.* **13**, 174.

The reagents used by the author are—

Barium peroxide, containing 63 % BaO_2.

Dilute sulphuric acid 1 : 2.

Arsenious acid dissolved in dilute hydrochloric acid, 5 gm. of pure As_2O_3 per litre.

Standard permanganate, 3·55 gm. per litre.

It was found that the relative strengths of the arsenic and permanganate solutions, when titrated together, diluted, and boiling, were, 18·2 c.c. of the latter to 20 c.c. of the former. Therefore 1 c.c. of permanganate by calculation = 0·00888 gm. Br.

The author found that treating 2 gm. of KCl in the apparatus, without bromine, always gave a faint trace of Cl, so that only 18 c.c. of permanganate were required for the 20 c.c. of arsenic, instead of 18·2 c.c. ; and this he regards as a constant for that quantity of material. The examples of analysis with from 0·05 to 0·2 gm. KBr, and all with the correction of 0·2 c.c., are satisfactory.

Norman McCulloch* has described a method, devised by himself, for the rapid and accurate determination of bromine, in presence of iodine or chlorine, in any of the ordinary commercial forms or chemical combinations free from oxidizing and reducing agents and metals forming bromides insoluble in hydrochloric acid. The author's explanation of the principles upon which the method is based is complicated and voluminous, and to this the reader is referred. I have not been able to verify the method, but as the author is known to have practical experience, as well as theoretical knowledge, a short summary is given here.

The solutions described by the author are—

Standard permanganate, 3·19 gm. per litre;

Standard potassium iodide, 8·278 per litre.

The solutions should agree volume for volume, but it is preferable to verify them by dissolving 2-3 gm. of iodine in caustic soda, in a 150 c.c. stoppered bottle, adding HCl in good excess, cooling, then adding the permanganate from a burette until nearly colourless. A little chloroform as indicator is then added, and the permanganate cautiously run in, with shaking, until the violet colour of the iodine is discharged, owing to production of ICl, due to the reaction of Cl liberated by the permanganate from HCl. The iodine equivalent of the permanganate is calculated to bromine by the coefficient × 0·6713 and each c.c. permanganate should represent about 0·004 gm. of Br.

The other reagents are:—Chloroform, purified by adding some permanganate, then HCl till the colour is discharged, then a little KI and the I so liberated again discharged with permanganate, the chloroform being finally washed free from all acid;

A three per cent. solution of hydrocyanic acid, made by decomposing a solution of pure potassium cyanide with excess of HCl and adding permanganate till a faint pink colour remains. 40 gm. of KCN in 400 c.c. of water with 70 c.c. of HCl will give such a solution. Owing to its poisonous nature great caution must be used in making this solution, and to avoid as much as possible the evolution of prussic acid the temperature must be kept down by ice or a freezing

* *C. N.* **60**, 259.

mixture of nitre and sal ammoniac. If the cyanide contains, as is often the case, some alkali carbonate, this should be removed previously by $BaCl_2$, as otherwise CO_2 will be liberated and a loss of HCN occur. Finally the cool solution is rendered faintly pink with some permanganate;

Solution of manganous chloride, made by dissolving 500 gm. of $MnCl_2+4H_2O$ in 250 c.c. of warm water. This solution is used to prevent the liberation of free chlorine from the HCl in the analysis.

Method of Procedure: The weighed bromide, containing from 0·05 to 0·15 gm. of Br, is dissolved in 15 c.c. of water in a 150 c.c. stoppered bottle, and about 30 c.c. of the manganese solution added; permanganate is then run in in excess of the required quantity, and the bottle cooled rapidly to 10° C. by ice or a freezing mixture. When cooled, the bottle is shaken by a rotary motion, and about 15 c.c. of moderately strong HCl slowly added, with motion of the bottle to dissolve the manganic hydroxide, 2-4 c.c. of hydrocyanic solution are then delivered in, the bottle closed and returned to the cooling mixture for about half an hour. The liquid is then titrated with the standard potassium iodide, until nearly decolorized from the decomposition of the manganic chloride, and then slightly coloured from liberation of free I. Lastly, the slight excess of iodide is determined by adding a little chloroform, and the titration finished with permanganate. The bromine is calculated by taking the difference between the amounts of bromine, represented by total permanganate and iodide used. If iodine is present it is, of course, recorded as bromine, and its amount, if required, must be ascertained by some other method capable of its determination in the presence of bromine.

The author gives several very good results obtained with pure sodium bromide.

CADMIUM.

$Cd=112{\cdot}4$.

This metal may be determined, as may many others, by precipitating as sulphide and decomposing the sulphide with a ferric salt, the iron being reduced to the ferrous state in proportion to the amount of sulphide present.

Follenius has found that when cadmium is precipitated as sulphide in acid liquids the precipitate is apt to be contaminated to a small extent with salts other than sulphide. The separation as sulphide is best made by passing H_2S into the hot liquid which contains the cadmium, and which should be acidified with 10 per cent. of concentrated sulphuric acid by volume. From hydrochloric acid solutions the metal is only completely separated by H_2S when the hot solution contains not more than 5 per cent. of acid of sp. gr. 1·11, or 14 per cent. if the liquid is cold.

Ferric chloride is to be preferred for the decomposition of the cadmium sulphide, and the titration is carried out precisely as in the case of Zinc (q. v.).

P. von Berg* gives a good technical process for the determination of either cadmium or zinc as sulphide, by means of iodine, as follows:—

* *Z. a. C.* **26**, 23.

Method of Procedure: The washed sulphide of zinc or cadmium is allowed to drain upon the filter, and then transferred, together with the filter, to a stoppered flask containing 800 c.c. of water deprived of air by boiling and the passage of carbonic acid gas. The whole is well shaken in order to break up the precipitate and bring it into the most finely divided condition possible, so that the sulphide may not be protected from the action of the iodine by separated sulphur. A moderate quantity of hydrochloric acid is added, there being no necessity to entirely dissolve the sulphide, and then an excess of iodine solution of known strength. The residual free iodine is then titrated with thiosulphate without loss of time. The whole operation, from the transference of the sulphide to the flask to the final titration, occupies about five minutes, and gives results varying between 98·8 and 100·2 per cent. The reaction proceeds according to the equation, $ZnS + 2HCl + I_2 = ZnCl_2 + 2HI + S$.

CALCIUM.

$Ca = 40{\cdot}09$.

1 c.c. $^N/_{10}$ permanganate	$=0{\cdot}002805$ gm. CaO
,, ,,	$=0{\cdot}005005$ gm. $CaCO_3$
,, ,,	$=0{\cdot}00861$ gm. $CaSO_4 + 2H_2O$
,, normal oxalic acid	$=0{\cdot}02805$ gm. CaO
Cryst. oxalic acid $\times 0{\cdot}444$	$=$ CaO
Double iron salt $\times 0{\cdot}07143$	$=$ CaO

The determination of calcium alkalimetrically has already been described (p. 72), but that method is of limited application, unless calcium oxalate, in which form Ca is generally separated from other bases, be converted into carbonate or oxide by ignition, and thus determined with normal nitric acid and alkali. This and the following method by Hempel are as exact in their results as the determination by weight; and where a series of determinations have to be made, the method is very convenient.

Titration with Permanganate.—The readiness with which calcium can be separated as oxalate facilitates the use of this method, so that it can be applied successfully in a great variety of instances. It is not necessary here to enter into detail as to the method of precipitation; except to say that it may take place in either ammoniacal or weak acetic acid solution, and that it is absolutely necessary to remove all excess of ammonium oxalate from the precipitate by washing with warm water previous to titration.

Method of Procedure: When the clean precipitate is obtained, a hole is made in the filter, and the bulk of the precipitate is washed through the funnel into a flask; the filter is then treated with small quantities of hot dilute sulphuric acid, and again washed into the flask. Hydrochloric acid in moderate quantity may safely be used for the solution of the oxalate, since there is not the danger of liberating free chlorine which exists in the case of iron (Fleischer, *Titrirmethode*, p. 76), but sulphuric is better.

When the precipitate is completely dissolved, the solution is freely diluted with water, and further acidified with sulphuric acid, warmed to 60° or 70°, and the standard permanganate cautiously delivered into the liquid with constant

agitation until a faint permanent pink tinge occurs, precisely as in the case of standardizing permanganate with oxalic acid (p. 123).

Procedure for Lime in Blast Furnace Slags: Place about 1 gm. of the very finely-ground slag into a beaker, cover with water, and boil gently, then add gradually strong HCl until the whole is dissolved, including SiO_2. Dilute the liquid, nearly neutralize with ammonia, and add a solution of ammonium acetate. The silica and alumina form a flocculent precipitate which is easily washed on a filter. The filtrate and washings are concentrated somewhat, and the CaO precipitated with ammonium oxalate and free ammonia; the precipitate is dissolved as before described in hot dilute sulphuric acid, and titrated with permanganate. If much manganese is present, the calcium oxalate must be re-dissolved and re-precipitated before the titration is made.

In all cases where a clean oxalate precipitate can be obtained, such as mineral waters, manures, etc., very exact results are obtainable; in fact, quite as accurate as by the gravimetric method. Ample testimony on this point is given by Fresenius, Mohr, Hempel, and others. When much iron, alumina, magnesia, etc., is present, it will be preferable to re-precipitate the oxalate, so as to free it from adhering contaminations previous to titration.

Indirect Titration.—In the case of calcium salts soluble in water and of tolerably pure nature, the determination by permanganate can be made by adding to the solution a measured excess of normal oxalic acid, then ammonia in slight excess, and heating to boiling, so as rapidly to separate the precipitate. The mixture is then cooled, diluted to a measured volume, filtered through a dry filter, and an aliquot portion titrated with permanganate, after acidifying with sulphuric acid as usual. A great variety of calcium salts may be converted into oxalates by a short or long treatment with oxalic acid or ammonium oxalate, including calcium sulphate, phosphate, tartrate, citrate, etc.

CERIUM.

$Ce = 140{\cdot}25.$

Stolba* states that the moist cerium oxalate may be titrated precisely as in the case of calcium oxalate with permanganate, and with accurate results. No examples or details, however, are given. It is probable that it is only correct in the case of the pure substance.

This method has, however, been examined by P. E. Browning and A. Lynch,† who prepared the oxalate from pure cerium chloride by ammonium oxalate. Definite volumes of the cerium solution, the exact strength of which was known (from 0·1 to 0·2 gm. of $CeCl_3$), were used for precipitation at a moderate temperature, some trials being made on neutral portions and some on portions

* *Z. a. C.* **19**, 194. † *Amer. Journ. Science*, **8**, No. 48.

slightly acid with HCl (in which case about 1 gm. of manganous sulphate was used). The precipitate, after being carefully washed, was dissolved in about 10 c.c. of hot dilute H_2SO_4, and then made up to about 500 c.c. with hot water at about 80° C. when the titration with permanganate was immediately made. The results obtained were, both in the neutral and acid solutions, very near the amounts of cerium taken.

Bunsen's method, originated many years ago, showed that the oxide of cerium obtained by ignition of the oxalate might be determined volumetrically by dissolving it in strong HCl with a few crystals of KI in a small sealed flask, which was heated on a water-bath till the oxide was dissolved and the free iodine liberated. The iodine was then titrated with thiosulphate in the usual way and the amount of cerium calculated therefrom.

$$1 \text{ c.c. } ^{N}/_{10} \text{ thiosulphate} = 0{\cdot}017225 \text{ gm. } CeO_2.$$

A modification of this method was adopted with satisfactory results by Browning, Hanford, and Hall, as follows :—

METHOD OF PROCEDURE: Weighed portions of the pure cerium dioxide, about 0·1 to 0·15 gm., were placed in small glass-stoppered bottles of about 100 c.c. capacity, together with 1 gm. of potassium iodide free from iodate and a few drops of water to dissolve the iodide. A current of CO_2 was passed into the bottle for about five minutes to expel the air, 10 c.c. of pure strong HCl were added, the stopper inserted, and the bottle heated gently upon a steam radiator for about one hour, until the dioxide dissolved completely and the iodine was set free. After cooling the bottle, to prevent loss of iodine upon removing the stopper, the contents were carefully washed into about 400 c.c. of water, and titrated with $^{N}/_{10}$ sodium thiosulphate to determine the amount of iodine liberated according to the reaction—

$$2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 2KCl + 4H_2O + I_2.$$

A few blank determinations were carried through in the bottles without the cerium dioxide to determine the amount of iodine set free under these conditions. The amount obtained was uniformly equal to 0·04 c.c. of the $^{N}/_{10}$ thiosulphate solution, which was taken as the correction and applied to all the determinations.

Determination in the Presence of other Rare Earths. G. von Knorre.* This is based on the fact that the yellow ceric salts are reduced by hydrogen peroxide in the presence of free acid to colourless cerous salts, as in the equation :

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2.$$

The cold solution of the ceric salt is mixed with an excess of a dilute solution of hydrogen peroxide, of which the strength is known, and when all colour has disappeared the excess of peroxide is titrated back with permanganate.

If the permanganate be standardized on iron, the amount of cerium present may be expressed in terms of iron, 55·85 parts of the latter being equivalent to 140·25 parts of cerium. It is advisable to use a dilute solution of permanganate (not more than 2 gm. of $KMnO_4$ per litre).

Notwithstanding Rose's statement that permanganate is slowly decolorized by a solution of cerous sulphate, the author finds that the end-reaction can be readily recognised. With a freshly prepared acidified solution of a ceric salt the reduction takes place instantaneously, but if the solution has been exposed to the air for some time, as long as fifteen minutes may be necessary for complete decolorization. The results obtained, however, in both cases are identical. By boiling an old solution after the addition of sulphuric acid, and cooling before

* *Z. a. C.*, 1897, 685–688.

adding the hydrogen peroxide, the rate of reduction is accelerated, and the reaction takes place almost as rapidly as in a freshly prepared solution.

Either sulphuric or nitric acid may be used, but it is essential that the acidification shall take place before the addition of the hydrogen peroxide, since otherwise by-reactions occur and the results are too high.

A method of Gibbs* is modified by Job† as follows :—

A known volume of the cerium solution is treated in the cold with peroxide of lead, and a large excess of concentrated nitric acid, in order to oxidize any cerous salts present, then the mixture is agitated, filtered, and the filtrate titrated with dilute hydrogen peroxide. The determination of cerium by this method may be carried out equally well in presence of thorium, lanthanum, and didymium, and should thus be of great use in directly determining cerium in the crude oxalates from monazite sand.

CHLORINE.

$Cl = 35{\cdot}46$.

1 c.c. $^N/_{10}$ silver solution $= 0{\cdot}003546$ gm. Cl.
,, ,, $= 0{\cdot}005846$ gm. NaCl.

THE powerful affinity existing between chlorine and silver in solution, and the ready precipitation of the resulting chloride, seem to have led to the earliest important volumetric process in existence, viz., the assay of silver by the wet method of Gay Lussac. The details of the process are more particularly described under the article relating to the assay of Silver q.v.; the determination of chlorine is just the converse of the process there described, and the same precautions, and to a certain extent the same apparatus, are required.

The solutions required, however, are systematic, and for exactness and convenient dilution are of decinormal strength as described on p. 141. In many cases it is advisable to possess also centinormal solutions, made by diluting 100 c.c. of $^N/_{10}$ solution to 1 litre.

1. Direct Precipitation with $^N/_{10}$ Silver solution.

Very weak solutions of chlorides, such as good drinking waters, are not easily examined for chlorine by direct precipitation, unless they are considerably concentrated by evaporation previous to treatment, owing to the fact that, unless a tolerable quantity of chloride can be formed, it will not collect together and separate so as to leave the liquid clear enough to tell whether on the addition of fresh silver a distinct formation of chloride occurs. The best effects are produced when the mixture contains chlorine equal to from $1\frac{1}{2}$ to 2 gm. of salt per 100 c.c. Should the proportion be much less than this, the difficulty of precipitation may be overcome by adding a quantity of freshly precipitated chloride, made by mixing equal volumes of $^N/_{10}$ salt and silver solutions, shaking vigorously, pouring off the clear liquid, and adding the chloride to the mixture under titration. The best vessel to use for the trial is a well stoppered round white bottle, holding from 100 to 150 c.c., and fitting into a paper case, so as to prevent access of strong light during the titration. Supposing, for instance, a neutral solution of potassium chloride requires titration, 20 or 30 c.c. are measured into the shaking bottle, a few drops of strong nitric acid added (free acid must

* *Z. a. C.*, 1864, p. 3[illegible]5. † *Compt. Rend.*, 1899, p. 101.

always be present in direct precipitation), and a round number of c.c. of silver solution added from the burette. The bottle is placed in its case (or may be enveloped in a dark cloth) and vigorously shaken for half a minute, then uncovered, and gently tapped upon a table or book, so as to start the chloride downward from the surface of the liquid where it often swims. A quick clarification indicates excess of silver. The nearer the point of exact counterbalance the more difficult to obtain a clear solution by shaking, but a little practice soon accustoms the eye to distinguish the faintest precipitate.

In case of overstepping the balance in any trial, it is only necessary to add to the liquid under titration a definite volume of $^{N}/_{10}$ salt solution, and finish the titration in the same liquid, deducting, of course, the same number of c.c. of silver as has been added of salt solution.

Fuller details and precautions are given under Silver.

2. Precipitation by $^{N}/_{10}$ Silver in Neutral Solution with Chromate Indicator (see p. 142.)

3. Titration with $^{N}/_{10}$ Silver and Thiocyanate (see p. 145).

This method gives very accurate results if, after the chlorine is precipitated with excess of $^{N}/_{10}$ silver, the silver chloride is filtered off, washed well, and the filtrate and washings titrated with $^{N}/_{10}$ thiocyanate for the excess of silver.

METHOD OF PROCEDURE: The material to be titrated, such as water residues, beer ash, or other substances in which the chlorine is to be determined, being brought into clear solution, a known volume of $^{N}/_{10}$ silver in excess is added, the mixture having been previously acidified with nitric acid; the mixture is well stirred, and the supernatant liquid filtered off through a small filter, the chloride well washed, and to the filtrate and washings 5 c.c. of ferric indicator (p. 146) and the same volume of nitric acid (p. 146) are added. The flask is then brought under the thiocyanate burette, and the solution delivered in with a constant gentle movement of the liquid until a permanent light-brown colour appears. If the silver chloride is not removed from the liquid previous to titration a serious error may occur, owing to the ready solubility of the chloride in the thiocyanate solution.

4. By Distillation and Titration with Thiosulphate or Arsenite.

In cases where chlorine is evolved directly in the gaseous form or as the representative of some other body (see p. 135), a very useful absorption apparatus is shown in fig. 38. The little flask *a* is used as a distilling vessel, connected with the bulb tubes by an india-rubber joint;* the stoppers for the tubes are also of the same material, the whole of which should be cleansed from sulphur by boiling in weak alkali. A fragment of solid magnesite may with advantage be added to the acid liquid in the distilling flask; in all other respects the process is conducted exactly as is described on p. 135 et seq.

* India-rubber and especially vulcanized rubber is open to some objection in these analyses, and apparatus is now readily to be had with glass connections.

This apparatus is equally well adapted to the absorption of ammonia or other gases, and possesses the great recommendation that there is scarcely a possibility of regurgitation.

Mohr's apparatus (fig. 39), is also serviceable for this method.

CHLORINE GAS AND BLEACHING COMPOUNDS.

1 c.c. $^N/_{10}$ sodium arsenite or thiosulphate solution = 0·003546 gm. Cl.

1 litre of chlorine at 0° C., and 760 mm., weighs 3·219 gm.

CHLORINE water may be titrated with thiosulphate by adding a measured quantity of it to a solution of potassium iodide, then delivering the thiosulphate from a burette till the colour of the free iodine has disappeared ; or by using an excess of the reducing agent, then starch, and titrating residually with $^N/_{10}$ iodine. When arsenious solution is used for titration, the chlorine water is delivered into a solution of sodium carbonate, excess of arsenious solution added, then starch and $^N/_{10}$ iodine till the colour appears, or iodized starch-paper may be used.

Bleaching Powder.—This important substance, which is also called *chloride of lime*, is made by the action of chlorine gas on slaked lime. Its composition appears to be best represented by the formula Ca (OCl) Cl,* which is due to Odling. When treated with water, it is resolved into calcium chloride and hypochlorite, thus :—

$$2Ca\ (OCl)\ Cl = CaCl_2 + Ca\ (OCl)_2.$$

The calcium hypochlorite constitutes the bleaching agent.

The technical analysis is confined to the determination of the "available" or "bleaching" chlorine, which in England and America is always expressed as percentage by weight on the bleaching powder. In France, however, its strength is given in Gay-Lussac degrees, which indicate the number of litres of chlorine gas, at 0° C. and 760 mm., capable of being evolved from one kilogram of bleaching powder.

100 French Degrees = 31·78 per cent. chlorine.

1. Titration by Arsenious Solution (Penot).

The first thing to be done in determining the value of a sample of bleaching powder is to bring it into solution, which is best managed as follows :—

The sample is well and quickly mixed, and 7·09 gm. weighed, put into a mortar, a little water added, and the mixture rubbed to a smooth cream ; more water is then stirred in with the pestle, allowed to settle a little while, then poured off into a litre flask ; the sediment again rubbed with water, poured off, and so on repeatedly, until the whole of the chloride has been conveyed into the

*Calcium chloro-hypochlorite.

flask without loss, and the mortar washed quite clean. The flask is then filled to the mark with water, well shaken, and 50 c.c. of the milky liquid (=0·3546 gm. bleaching powder) taken out with a pipette, emptied into a beaker, and the $^{N}/_{10}$ arsenious solution delivered in from a burette until a drop of the mixture taken out with a glass rod and brought in contact with iodized starch-paper (p. 140) gives no blue stain.

The starch-paper may be dispensed with by adding arsenious solution in excess, then starch, and titrating residually with $^{N}/_{10}$ iodine till the blue colour appears. The number of c.c. of arsenite used gives percentage of available chlorine (35 % available chlorine is a common guarantee).

2. Bunsen's Method.

10 or 20 c.c. of the chloride of lime solution, prepared as above, are measured into a beaker, and an excess of solution of potassium iodide added; the mixture is then diluted somewhat, acidified with acetic acid, and the liberated iodine titrated with $^{N}/_{10}$ thiosulphate and starch; 1 eq. iodine so found represents 1 eq. chlorine.

The presence of chlorate does not affect the result when acetic acid is used. If it be desired to determine the amount of chlorate in bleach, the following method has been devised by R. Fresenius. It depends on the fact that hypochlorites are decomposed by lead acetate with formation of lead peroxide, whilst the chlorate which may be present is unaffected.

Method of Procedure: 20 gm. of bleaching powder are ground up with water in repeated quantities and made up to a litre; after settling, 50 c.c. (=1 gm. of bleach) are filtered off through a dry filter, put into a flask, and mixed with a solution of lead acetate in some excess. There is formed at first a white precipitate of lead chloride and lead hydroxide; these being acted on by the hypochlorite become first yellow, then brown, with liberation of chlorine and passing into lead peroxide. After the precipitate has settled, more lead solution is added, to make sure that the conversion is complete. The mixture is allowed to stand in the open flask, with frequent shaking, till all smell of chlorine has disappeared, which occurs in from eight to ten hours. The precipitate is then filtered off and washed till the wash-water is free from acid. The washings are evaporated somewhat, added to the filtrate, and the whole mixed with sodium carbonate in slight excess, to precipitate the lead and lime as carbonates—these are well washed, the filtrate and washings, which contain the chlorate as the sodium salt, evaporated nearly to dryness, then transferred to either a Fresenius or Mohr apparatus (fig. 38 or 39) and distilled with HCl as directed on p. 135 et seq. 1 eq. : $I = Cl_2O_5$.

Mixtures of Chlorides, Hypochlorites, and Chlorates.—It is known that chlorine acting upon alkali and alkaline-earthy hydrates gives rise to chlorides, and at the same time to chlorates, or to hypochlorites, according as the temperature and the concentration are higher or lower. Under average conditions the three kinds of salts are formed simultaneously.

A mixture of the same salts is produced if solutions of sodium chloride are submitted to electrolysis, according to the processes recently used for the manufacture of free chlorine and of caustic soda, or of chlorates, or hypochlorites.

In these various cases it is of great industrial importance to determine easily the proportion of each of the salts present.

For the analysis of such a mixture of salts, the subjoined method is recommended as at once expeditious and accurate. All the determinations are performed successively upon the same solution.*

METHOD OF PROCEDURE: 1. The mixture of hypochlorite, chlorate, and chloride is poured into a beaker. There is then run into it from a burette a standard solution of alkali arsenite until the hypochlorite is completely reduced. To find the exact moment when the reduction is completed, a drop of the liquid is placed upon a porcelain plate in contact with a drop of solution of potassium iodide and starch.

On the mixture of the two drops there appears a blue colour as long as there remains any hypochlorite not reduced. As soon as the mixture ceases to become coloured, the volume of the arsenite liquid is noted, and the proportion of hypochlorite or hypochlorous acid which has transformed it into arsenic acid is obtained; or consequently, that of the corresponding chlorine.

$$As_2O_3 + CaCl_2O_2 = As_2O_5 + CaCl_2.$$

or

$$As_2O_3 + 2NaClO = As_2O_5 + 2NaCl.$$

2. The liquid (which now contains merely chlorate and chloride) is slightly acidified with sulphuric acid, and a quantity of ammonium-ferrous sulphate added, at least twenty times as much as the chlorate supposed to be present. Heat to about 100°, adding in small successive quantities 5 c.c. of sulphuric acid diluted with 15 c.c. of water. It is best to use a tap-funnel, letting the acid fall in drop by drop. After having stoppered the vessel, to avoid contact of air, it is allowed to cool for a short time, and the excess of ferrous salt is then titrated with permanganate. As the quantity of ferrous salt which was introduced is known, by difference the quantity which has been peroxidized at the expense of the chlorate reduced to the state of chloride is found

$$NaClO_3 + 6FeO = NaCl + Fe_2O_3.$$

It is thus easy to calculate the proportion of chlorate or of chloric acid, or the corresponding quantity of chlorine.

3. The total chlorine, which is now present entirely, in the state of chloride, is determined as follows:—The rose tint produced by the permanganate is removed by adding a trace of ferrous sulphate. Then add a measured volume of standard silver nitrate, more than enough to precipitate all the chlorine, and determine the excess of the silver salt by means of standard thiocyanate (p. 145). The ferric salt previously formed by the peroxidation of the ferrous salt serves as an indicator, by producing a permanent red colouration as soon as there is no more silver salt to precipitate. The arsenic acid produced in the first operation does not interfere in the least.

In order to avoid the use of too large a quantity of silver nitrate, which would be necessary on account of the large proportion of chlorine to be precipitated, an aliquot part of the solution may be taken.

The chlorine found in the state of a chloride in the original liquid is easily calculated by deducting from the total chlorine just determined the two quantities already found in the state of hypochlorite and of chlorate.

The three operations succeed each other without interruption, and without separate preparation, and are completed in a short time.

In a number of experiments with mixtures, the discrepancies found between the experimental results and the calculated numbers rarely reached 1 mgm. when operating upon from 250 to 500 mgm.

Mixtures of Chlorides, Chlorates, and Perchlorates.—A. Carnot.† Perchlorates are found with chlorides and chlorates in the products of the calcination of chlorates. Hypochlorites are only produced in the cold or by wet methods; but in such cases no perchlorates are formed, nor can the latter be reduced by the usual reagents in solution, dry heat being necessary to accomplish this result.

* A. Carnot, *Compt. Rend.* **122**, 449. † *Compt. Rend.* **122**, 452.

In analysing such mixtures, the chlorides and chlorates are determined first by titrating one portion of the solution for the chlorides by Volhard's method, and the other part for the total chlorine after reduction of the chlorates by the aid of ferrous sulphate; or, as an alternative method, both titrations can be performed on the same liquid, the chlorides first—with sodium arsenate as indicator in preference to potassium chromate, which would interfere with the subsequent reaction—and then the total chlorine after reduction of the chlorates.

The perchlorates are determined by heating the powdered substance, mixed with four or five times its weight of purified quartz-sand, in a platinum crucible, the mixture being covered by a layer of the same sand 1 or 2 cm. deep. The bottom of the crucible is kept at a red heat for about twenty to thirty minutes, and this is sufficient completely to reduce the chlorates and perchlorates, volatilization of the chloride being prevented by the condensing effect of the upper layer of sand. An aqueous solution is then made, the total chlorides titrated as before, and the perchlorate found by difference.

Determination of Perchlorate in Chili Saltpetre.—Ahrens and Hett*. 20 gm. of the powdered sample are introduced into a flat 200 c.c. platinum dish, moistened with 2-3 c.c. of cold saturated caustic soda, 1 gm. of pure manganese dioxide added, and the whole evaporated to dryness; the dish is then covered and heated to redness. When cold, the fused mass is treated with 100 c.c. of hot water, allowed to cool, and then made up to 250 c.c.; 50 c.c of the filtrate are acidified with 10-15 c.c. of nitric acid of sp. gr. 1·20, and a solution of permanganate is added drop by drop until the colour is permanent for a minute, showing that all the nitrous acid has been oxidized. The chlorine is then determined by Volhard's process, and the difference between the amounts of chlorine found before and after fusion is calculated into perchlorate. Iodides present in the sample do not interfere, as they are oxidized to iodates by the permanganate.

The Iodimetric Determination of Chloric and Nitric Acids.—The following methods by McGowan† depend on the principle that when a fairly concentrated solution of a nitrate or chlorate is warmed with an excess of pure, strong hydrochloric acid, a nitrate is completely decomposed, and the production of nitrosyl chloride and chlorine is quantitative, the reaction being

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

If the operation is conducted in an atmosphere of carbonic acid, and the escaping gases are passed through a solution of potassium iodide, an amount of iodine is liberated exactly equivalent to the whole of the chlorine present (free and combined), nitric oxide escaping. 1 mol. of nitric acid thus yields 3 atoms of chlorine or iodine. The iodine can then be titrated in the usual manner with thiosulphate. With chlorates only chlorine is evolved. De Koninck and Nihoul‡ give details of a process depending upon the same principle.

Method of Procedure for Nitrates: It is, of course, absolutely essential that air should be completely excluded from the apparatus as, if any were present, the escaping nitric oxide would be re-oxidized to nitrogen trioxide or tetroxide, and this would in its turn liberate a further quantity of iodine from the iodine solution.

* *Chem. Centr.* 1898, **2**, 558. † *J. C. S.* **69**, 530 and *J. C. S.* **61**, 87.
‡ *Zeit. für angew. Chem.* August 15th, 1890.

The apparatus required is very simple, and can readily be made by any one moderately expert at glass-blowing. The main point to be attended to is to have no corks or rubber stoppers, etc., for the escaping chlorine to act upon. Fig. 41 is a sketch of the apparatus. The condensing arrangement for the chlorine does its work perfectly, and may therefore be used with advantage, not only for this, but also for other similar methods in which iodine is set free. The measurements given are those of the apparatus as used by the author.

A is a small, round-bottomed flask, into the neck of which a glass stopper, *x*, is accurately ground (with fine emery and oil). The capacity of the bulb is about 46 c.c., and the length of the neck, from *x* to *y*, 90 mm. The first condenser is a simple tube, slightly enlarged at the foot into two small bulbs. The length from *a* to *b* is 300 mm., from *b* to *e* 180 mm., and from *e* to *f* 30 mm. The capacity of the bulb *B* is 25 c.c., and the total capacity of the two bulbs and tube, up to the top of *C*, 41 c.c. This condenser is immersed, up to the level of *e* in a beaker of water. *D* is a Geissler bulb apparatus, and *E* a chloride of calcium tube, filled with broken glass, which acts as a tower, *g* is a small funnel, attached by rubber and lip to the branch tube *h*. Between the tube *i* and the wash-bottle for the carbonic acid is placed a short piece of glass tubing, *s*, containing a strip of filter-paper, slightly moistened with iodide of starch solution. This tube *s* is really hardly necessary, as no chlorine escapes backwards if a moderate current of carbonic acid is kept passing, but it serves as a check. The joints *p* and *q* are of narrow rubber tubing. The joint *o* is made by grinding one tube into the other. *k* is the outlet tube.

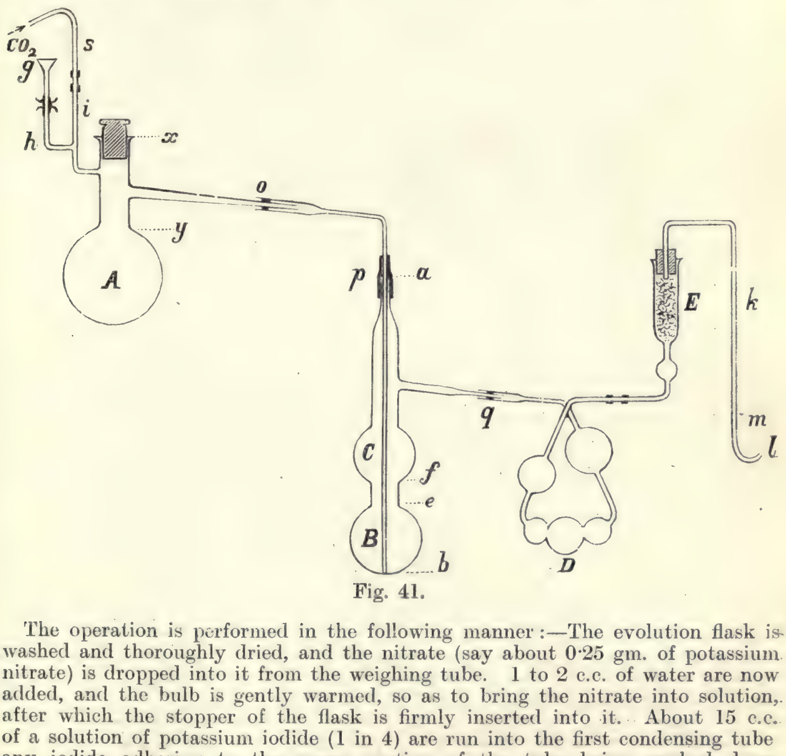


Fig. 41.

The operation is performed in the following manner:—The evolution flask is washed and thoroughly dried, and the nitrate (say about 0·25 gm. of potassium nitrate) is dropped into it from the weighing tube. 1 to 2 c.c. of water are now added, and the bulb is gently warmed, so as to bring the nitrate into solution, after which the stopper of the flask is firmly inserted into it. About 15 c.c. of a solution of potassium iodide (1 in 4) are run into the first condensing tube any iodide adhering to the upper portion of the tube being washed down with a little water, and 5 c.c. of the same solution, mixed with 8 to 10 c.c. of water, are sucked into the Geissler bulbs, whilst the glass in tower *E* is also

thoroughly moistened with the iodide. The Geissler bulbs should be so arranged that gas only bubbles through the last of them, the liquid in the others remaining quiescent.

All the joints having been made tight, the CO_2 is turned on briskly, and passed through the apparatus until a small tubeful collected at *l*, over caustic potash solution, shows that no appreciable amount of air is left in it. The small outlet tube *l* is now replaced by a chloride of calcium tube, filled with broken glass which has been moistened with the above iodide solution, and closed by a cork through which an outlet tube passes, the object of this "trap" tube being to prevent any air getting back into the apparatus; and the brisk current of CO_2 is continued for a minute or two longer, so as practically to expel all the air from this last tube. The stream of gas is now stopped for an instant, and about 15 c.c. of pure concentrated hydrochloric acid, free from chlorine, run into *A* through the funnel *g* (into the tube of which it is well to have run a few drops of water before beginning to expel the air from the apparatus), and *A* is shaken so as to mix its contents thoroughly. A slow current of CO_2 is now turned on again (1 to 2 bubbles through the wash-bottle per second), and *A* is gently warmed over a burner. It is a distinct advantage that the reaction does not begin until the mixed solutions are warmed, when the liquid becomes orange-coloured, the colour again disappearing after the nitrosyl chloride and chlorine have been expelled. The warming should be very gentle at first, in order to make sure of the conversion of all the nitric acid, and also because the first escaping vapours are relatively very rich in chlorine; after which the liquid in *A* is briskly boiled. A very little practice enables the operator to judge as to the proper rate of warming. When the volume of liquid in *A* has been reduced to about 7 c.c. (by which time it is again colourless), the stream of CO_2 is slightly quickened, and the apparatus allowed to cool down a little. The burner is now set aside for a few minutes, and 2 c.c., or so, more of hydrochloric acid previously warmed in a test-tube, run in gently through *g*; there is no fear either of the iodide solution running back, or of any bubbles of air escaping through *y*, if this is done carefully. This is a precautionary measure, in case a trace of the liberated chlorine might have lodged in the comparatively cool liquid in tube *h*. The CO_2 is once more turned on slowly, and the liquid in *A* is boiled again until it is reduced to about 5 c.c. It is now only necessary to allow the apparatus to cool down, passing CO_2 all the time, after which the contents of the condensers are transferred to a flask and titrated with thiosulphate. At the end of a properly conducted experiment, the glass in the upper part of tower *E* should be quite colourless, and there should only be a mere trace of iodine showing in the lower part of the tower, while the liquid in the last bulb of the Geissler apparatus ought to be only pale yellow. During the operation the stopper of *A* and the various joints can be tested for tightness from time to time by means of a piece of iodide of starch paper, and, before disjointing, it is well to test the escaping gas (say, at *m*) in the same way, to make sure that all nitric oxide has been thoroughly expelled.

EXAMPLE: 0·2627 gm. of pure KNO_3 was taken. The liberated iodine required 38·55 c.c. of thiosulphate (of which 1 c.c. =0·006805 gm. KNO_3) for conversion. This gave 0·2623 gm. nitrate found, or 99·86 per cent.

METHOD OF PROCEDURE FOR CHLORATES: The apparatus employed is the same as for nitrates, but since it is unnecessary in this determination previously to expel the air present by a current of CO_2, those tubes which come after the tower *E* are dispensed with. The details of the operation are also practically the same as in the case of a nitrate, only simpler. Comparatively dilute hydrochloric acid may be employed, and the CO_2 is required merely to ensure a regular passage of the vapours through the iodine solution, and to prevent any chlorine escaping backwards. This is tested, as before, by the small piece of iodide of starch paper in tube *s*, which should be so placed as never to get warm.

The chlorate is weighed out into the dry evolution flask *A*, then dissolved in 8 to 10 c.c. of water, and, after all the necessary connections have been made, 8 to 10 c.c. of pure concentrated hydrochloric acid are run in through the funnel *g*. Since the reaction begins in the cold, the CO_2 must be turned on immediately,

and kept passing at the rate of about four bubbles per second. Care should be taken to heat very gently at first, until the bulk of the chlorine has come over, after which the lamp flame may be gradually turned up and the liquid boiled, exactly as in the case of the nitrate; this ensures that no chlorine escapes backwards. And, as before, after all the chlorine has been apparently driven out, and the solution has become colourless, a second quantity of warm hydrochloric acid (1 in 2) is run in, and the boiling repeated for a few minutes.

Chlorates, Iodates, and Bromates.

$Cl_2O_5 = 150{\cdot}92$. $I_2O_5 = 333{\cdot}84$. $Br_2O_5 = 239{\cdot}84$. The compounds of chloric, iodic, and bromic anhydrides may all be determined by distillation or digestion with excess of hydrochloric acid; with chlorates the quantity of acid must be considerably in excess.

In each case 1 eq. of the respective anhydrides taken as monobasic, or their compounds, liberates 6 eq. of chlorine, and consequently 6 eq. of iodine when decomposed in the digestion flask. In the case of distillation, however, iodic and bromic acids only set free 4 eq. iodine, while iodous and bromous chlorides remain in the retort. In both these cases digestion is preferable to distillation.

EXAMPLE: 0·2043 gm. pure potassium chlorate, equal to the sixth part of $\frac{1}{10000}$ eq., was decomposed by digestion with potassium iodide and strong hydrochloric acid in the bottle shown in fig. 40. After the reaction was complete and the bottle cold, the stopper was removed and the contents washed out into a beaker, starch added, and 103 c.c. $^N/_{10}$ thiosulphate delivered in from the burette; then again 23·2 c.c. of $^N/_{100}$ iodine solution, to reproduce the blue colour; this latter was therefore equal to 2·32 c.c. $^N/_{10}$ iodine, which deducted from the 103 c.c. thiosulphate gave 100·68 c.c., which multiplied by the factor 0·002043, gave 0·2056 gm., instead of 0·2043 gm.

CHROMIUM.

$Cr = 52$.

1. Reduction by Iron.

THE determination of chromates is very simply and successfully performed by the aid of ferrous sulphate, being the converse of the process devised by Penny for the determination of iron (see p. 126).

METHOD OF PROCEDURE: A very small beaker or other convenient vessel is partly or wholly filled, as may be requisite, with perfectly dry and granular double sulphate of iron and ammonia; the exact weight then taken and noted. The chromium compound is brought into solution, not too dilute, acidified with sulphuric acid, and small quantities of the iron salt added from time to time with a dry spoon, taking care that none is spilled, and stirring with a glass rod, until the mixture becomes green and the iron is in excess, best shown by a small drop being brought in contact with a drop of potassium ferricyanide, when, if a blue colour appears at the point of contact, the iron is in excess. It is necessary to determine this excess, which is most conveniently done by $^N/_{10}$ dichromate being added until the blue colour produced by contact with the indicator disappears. The vessel containing the iron salt is again weighed, the loss noted; the quantity of the salt represented by the $^N/_{10}$ dichromate deducted from it, and the remainder multiplied by the factor required by the substance sought. A freshly made standard solution of iron salt, well acidified with sulphuric acid, may be used in place of the dry salt.

EXAMPLE: 0·5 gm. pure potassium dichromate was taken for analysis, and to its acid solution 4·15 gm. double iron salt added. 3·3 c.c. of $^N/_{10}$ dichromate were required to oxidize the excess of iron salt; it was found that 0·7 gm. of the salt =17·85 c.c. dichromate, consequently 3·3 c.c. of the latter were equal to 0·1299 gm. iron salt; this deducted from the quantity originally used left 4·0201 gm., which multiplied by 0·1255 gave 0·504 gm. instead of 0·5 gm.

In the case of lead chromate being determined in this way, it is best to mix both the chromate and the iron salt together in a mortar, rubbing them to powder, adding hydrochloric acid, stirring well together, then diluting with water and titrating as before. Where pure double iron salt is not at hand, a solution of iron wire in sulphuric acid, freshly made, and of ascertained strength, may be used.

2. Determination of Chromates by Distillation with Hydrochloric Acid.

When chromates are boiled with an excess of strong hydrochloric acid in one of the apparatus (fig. 38 or 39), every 1 eq. of chromic acid liberates 3 eq. chlorine. For instance, with potassium dichromate the reaction may be expressed as follows—

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Cl_2.$$

If the liberated chlorine is conducted into a solution of potassium iodide, 3 eq. of iodine are set free, and can be determined by $^N/_{10}$ arsenite or thiosulphate. 3 eq. of iodine so obtained (=380·76) represent 1 eq. chromic acid (=100). The same decomposition takes place by mere digestion, as described on page 138.

3. Chrome Iron Ore, Steel, etc.

The ore varies in quality, some samples being very rich in chromium, while others are very poor. In all cases the sample is to be first of all brought into *extremely fine powder*. About a gram is rubbed tolerably fine in a steel mortar, then finished fractionally in an agate mortar.

Christomanos recommends that the coarse powder should be ignited for a short time on platinum previous to powdering with the agate mortar; after that it should be sifted through the finest material that can be used, and the coarser particles returned to the mortar for regrinding.

Previous to analysis it should be again ignited, and the analysis made on the dry sample.

O'Neill's Process.—The very finely powdered ore is fused with ten times its weight of potassium bisulphate for twenty minutes, taking care that it does not rise over the edge of the platinum crucible; when the fusion is complete, the molten mass is caused to flow over the sides of the crucible, so as to prevent the formation of a solid lump, and the crucible set aside to cool. The mass is transferred to a porcelain dish, and lixiviated with warm water until entirely dissolved (there must be no black residue, otherwise the ore is not completely decomposed); sodium

carbonate is then added to the liquid until it is strongly alkaline; it is then brought on a filter, washed slightly, and the filter dried. When perfectly dry, the precipitate is detached from the filter as much as possible; the filter burned separately; the ashes and precipitate mixed with about twelve times the weight of the original ore of a mixture of two parts potassium chlorate and three parts sodium carbonate, and fused in a platinum crucible for twenty minutes or so; the resulting mass is then treated with boiling water, filtered, and the filtrate titrated for chromic acid as in (1)

The ferric oxide remaining on the filter is titrated, if required, by any of the methods described under Iron.

Britton's Process.—Reduce the mineral to the finest possible state of division in an agate mortar. Weigh off 0·5 gm., and add to it 4 gm. of flux, previously prepared, composed of one part potassium chlorate and three parts soda-lime; thoroughly mix the mass by triturating in a porcelain mortar, and then ignite in a covered platinum crucible at a bright-red heat for an hour and a half or more. 20 minutes is sufficient with the gas blowpipe. The mass will not fuse but when cold can be turned out of the crucible by a few gentle taps, leaving the interior of the vessel clean and bright. Triturate in the mortar again and transfer the powder to a tall beaker, add about 20 c.c. of hot water, and boil for two or three minutes; when cold add 15 c.c. of HCl, and stir with a glass rod, till the solid matter, with the exception probably of a little silica in flakes, becomes dissolved. Both the iron and chromium will then be in the highest state of oxidation—Fe_2O_3 and Cr_2O_3. Pour the fluid into a white porcelain dish, and dilute with washings of the beaker to about 100 c.c. Immediately after, add cautiously 1 gm. of metallic iron of known purity, or an equivalent quantity of double iron salt previously dissolved in dilute sulphuric acid, and further dilute with cold water to about 150 c.c. Titrate with $^{N}/_{10}$ permanganate the amount of ferrous oxide remaining. The difference between the amount of iron found and of the iron weighed will be the amount oxidized to sesquioxide by the chromic acid. Every one part so oxidized will represent 0·31035 of Cr or 0·45359 of Cr_2O_3, in which last condition the substance usually exists in the ore.

If the amount of iron only in the ore is to be determined, the process is still shorter. After the fluxed mineral has been ignited and reduced to powder as already directed, dissolve it by adding first, 10 c.c. of hot water and applying a gentle heat, and then 15 c.c. of HCl, continuing the heat to incipient boiling till complete decomposition has been effected; cool by immersing the tube in a bath of cold water, add pieces of pure metallic zinc sufficient to bring the iron to the condition of protoxide and the chromium to sesquioxide, and apply heat till small bubbles of hydrogen cease and the zinc has become quite dissolved; then nearly fill the tube with *cold* water, acidulated with one-tenth of sulphuric acid, and pour the contents into the porcelain dish, add *cold* water to make up the volume to about 250 c.c., and titrate with standard permanganate or dichromate.

Sell's Process.—This method* is carried out by first fusing the finely ground ore with a mixture of sodium bisulphate and fluoride in the proportion of 1 mol. bisulphate and 2 mol. fluoride, and subsequent titration of the chromic acid by standard thiosulphate and iodine.

From 0·1 to 0·5 gm. of the ore is placed on the top of ten times its weight of the above-mentioned mixture in a large platinum crucible, and ignited for fifteen minutes; an equal weight of sodium bisulphate is then added, and well incorporated by fusion and stirring with a platinum wire; then a further like quantity of bisulphate added in the same way. When complete decomposition has occurred, the mass is boiled with water acidulated with sulphuric acid, and the solution diluted to a definite volume according to the quantity of ore originally taken.

* *J. C. S.* 1879, p. 292.

To ensure the oxidation of all the chromium and iron previous to titration, a portion, or the whole, of the solution is heated to boiling, and permanganate added until a permanent red colour is produced. Sodium carbonate is then added in slight excess, and sufficient alcohol to destroy the excess of permanganate; the manganese precipitate is then filtered off, and the clear solution titrated with $^N/_{10}$ thiosulphate and iodine.

The author states that the analysis of an ore by this method may be accomplished in one hour and a half.

For the oxidation of salts of chromium, the same authority recommends boiling with potash or sodium carbonate (to which a small quantity of hydrogen peroxide is added) for 15 minutes.

For the preliminary fusion and oxidation of chrome iron ore, Dittmar recommends a mixture of two parts borax glass and one and a half part each of sodium and potassium carbonates. These are fused together in a platinum crucible until all effervescence ceases, then poured out into a large platinum basin or upon a clean iron plate to cool, broken up, and preserved for use.

Ten parts of this mixture are used for one part of chrome ore, and the fusion made in a platinum crucible, closed for the first five minutes, then open for about forty minutes, frequently stirring with a platinum wire, and using a powerful Bunsen flame. The gas blowpipe hastens this method considerably.

The above described methods of treating the ores of chromium so as to obtain complete decomposition are apparently now superseded to a great extent by the use of sodium peroxide, but the action of this reagent upon platinum, gold, silver, nickel, or porcelain is so energetic that its use requires great care. Many well known authorities on the analysis of chrome ores use a basic mixture such as was first suggested by Clark, but modified by Stead, *i.e.*, magnesia or lime four parts, potassium and sodium carbonates of each one part. Clark's original mixture of magnesia and caustic soda acts on platinum, but Stead's mixture does not.

The fusion is made by mixing the very finely ground sample with ten times its weight of the basic mixture in a platinum crucible, and heating to bright redness at the back of a gas muffle for about an hour. When the crucible is removed and cool the mass is found sintered together. It is removed to a beaker, and the crucible washed out with water and dilute sulphuric acid. The decomposition is generally complete, but if any black specks are found they must be separated by filtration, dried, and again fused with some of the basic mixture; finally the whole is mixed with excess of ferrous salt, and the unoxidized iron titrated with dichromate as before described

Rideal and Rosenblum* give a series of experiments on the determination of chromium in ores, steels, etc., and on the use of sodium peroxide, which latter they find has a most destructive effect on all kinds of vessels in which the decomposition is made. Nickel seems the best material if not exposed to too high a temperature, but they found also that a good deal of nickel was dissolved from the crucibles by the sulphuric acid used to dissolve the melt, and they therefore attach great importance to the filtration of the

* *J. S. C. I.* **14**. 1017.

aqueous solution of the melt, so as to remove nickel and iron oxides, which otherwise interfere with the titration by masking the colour of the indicator.

Ferrochrome, Chromium Steel, etc.—Spüller and Brenner* describe an improved method which gives better results than the previous method advocated by Spüller and Kalman.

METHOD OF PROCEDURE FOR FERROCHROME: 0·35 gm. of the finely powdered sample, mixed in a silver dish with 2 gm. of dry powdered sodium hydroxide and covered with 4 gm. of sodium peroxide, is heated until the mixture begins to melt, when, as a consequence of the strong chemical action, the whole mass soon becomes liquefied. The dish is then again heated for ten minutes over a powerful burner, and 5 gm. of sodium peroxide is cautiously added, stirring all the while with a silver spatula. After heating for thirty minutes more, another 5 gm. of sodium peroxide is added and the heating continued for twenty minutes, when a final 5 gm. of the peroxide is added.

When cold, the silver basin is placed in a deep porcelain dish and filled with water; when the lixiviation is completed, which takes a few minutes only, the silver dish is lifted out and well rinsed with hot water. A brisk current of CO_2 is then passed through the liquid for half an hour, the whole allowed to cool, introduced into a litre measure, and made up to the mark with water. After shaking and filtering, 250 c.c. are taken and the chromic acid titrated by a permanganate solution of which 1 c.c. equals about 0·005 gm. of iron, and a solution of ferrous ammonium sulphate containing 7 gm. of the salt in 500 c.c. The chromium solution is diluted with 1 litre of cold water which has been previously boiled and acidified with 20 c.c. of sulphuric acid (1 : 5 by volume); 100 c.c. of ferrous ammonium sulphate are added, and the mixture titrated back with permanganate. The strength of the ferrous solution is determined by a blank experiment under similar conditions. If the solution of the melt appears green, it is advisable to add first a few c.c. of permanganate and then some more sodium peroxide, when a pure yellow liquid will be obtained.

METHOD OF PROCEDURE FOR CHROME STEEL: 2 gm. of the sample is dissolved in 20 c.c. of warm hydrochloric acid contained in a porcelain dish, 10 c.c. of dilute sulphuric acid (1 : 1) are added, and the whole evaporated to dryness; the residue is then transferred to a silver dish and heated with 2 gm. of sodium hydroxide and 5 gm. of sodium peroxide, until the sulphates are decomposed and the mass begins to cake. A strong heat is now applied and another 5 gm. of the peroxide is added. When the mass begins to fuse, it is well stirred with a silver spatula, and after 20 minutes another 5 gm. of peroxide is added; after another 20 minutes, when the oxidation is complete, a further addition of 5 gm. of the soda is made and the mass is allowed to cool. The melt is then extracted as in the former case, but the liquid is made up to 500 c.c. only, and 250 c.c. of the filtre (=1 gm. of sample) are taken for the titration of the chromium. In this case, the authors prefer titrating according to Zulkowsky's method, *i.e.*, the liquid is put into a tall, narrow beaker, mixed with 10 c.c. of a 10 per cent. solution of potassium iodide, and acidified with pure hydrochloric acid. To another beaker containing 20 c.c. of a solution of potassium dichromate (0·9833 gm. per litre), 250 c.c. of water are added, then 10 c.c. of a 10 per cent. solution of potassium iodide and a little hydrochloric acid. After being left for 15 minutes in a dark place, both liquids are titrated with solution of sodium thiosulphate containing 4·96 gm. of the salt per litre. The amount of chromium being known in the one solution, the quantity contained in the other is readily calculated.

Rideal and Rosenblum have obtained excellent results with ferrochrome by fusion with sodium peroxide alone. The manner of procedure was as follows:—

* *Chem. Zeit.*, 1897. 2, p. 3, 4.

About 0·5 gm. of a very finely powdered ferrochrome was mixed with 3 gm. of sodium peroxide and heated very gently in a nickel crucible, until the mass began to melt, and then to glow by itself. The heating was then continued for ten minutes, and after the mass was partially cooled 1 gm. of sodium peroxide was added and the heating continued for another five minutes.

The crucible, when still moderately warm, was placed in a suitable porcelain basin, which was then half filled with hot water and covered with a clock glass. The melt easily dissolved in the hot water, the solution obtained being of a deep purple colour, due to sodium ferrate, which is abundantly formed during the fusion. The solution also contained sodium manganate, resulting from the oxidation of the manganese which is present in ferrochrome.

To decompose both these salts a small quantity of sodium peroxide was added, on which the solution immediately lost its purple colour. The solution was then boiled for ten minutes to decompose the excess of sodium peroxide, and the insoluble residue of iron, nickel, and manganese oxide was filtered off. An excess of sulphuric acid was then added to the solution, and after cooling it was titrated in the usual manner with permanganate.

Galbraith's method, modified somewhat by Stead*, is considered the most rapid method for the determination of chromium in irons and steels.

The sample (2 gm.) is dissolved in 30 c.c. dilute sulphuric acid (1 to 3), filtered, the solution diluted to about 300 c.c. and heated to boiling. Strong solution of potassium permanganate is now added until the red colour is permanent for ten minutes, then 80 c.c. of 10 per cent. hydrochloric acid, and the liquid heated until decolorized; 150 c.c. of water are added, about 100 c.c. boiled off to expel the chlorine, and the chromium is then titrated with ferrous sulphate and dichromate as on p. 126. The residue insoluble in dilute sulphuric acid is mixed with 0.5 gm. of the basic mixture previously mentioned, and heated to intense redness for half an hour; the chromium is afterwards titrated in hydrochloric acid solution with ferrous sulphate and dichromate.

Another process consists in dissolving 2 gm. of the sample in hydrochloric acid; without filtering, the liquid is nearly neutralized with a 2 per cent. solution of caustic soda, and, after diluting to 300 c.c., 10 c.c. of a 5 per cent. solution of sodium phosphate and 30 gm. of sodium thiosulphate are added. After boiling to expel the SO_2, 20 c.c. of a saturated solution of sodium acetate are added, and the boiling continued for five minutes; the precipitated chromium phosphate is then washed with a 2 per cent. solution of ammonium nitrate, dried, calcined, and fused with the basic mixture. The melt, dissolved in 30 c.c. of hydrochloric acid and 150 c.c. of water, is boiled for ten minutes and titrated. The process may be used in presence of vanadium. In this case, the chromium must be titrated by means of ferrous sulphate and permanganate in presence of sulphuric acid.

Rideal and Rosenblum's experiments appear to show that sodium peroxide, if certain conditions be observed in its use, is a very valuable reagent for the analysis of chrome ore, ferrochrome, and chrome steel, as it removes the two main defects of former methods, viz., the necessity of repeated fusion to effect complete decomposition and the inconvenient slowness of these processes. The conditions which should be observed are summarized by them as follows:—

(1) Great care should be taken to reduce the chrome ore or the ferrochrome to an almost impalpable powder. This can be done without much difficulty if the ore or the alloy be crushed in a steel mortar until a powder is obtained which will pass through a linen bag. This powder is then ground in an agate

* *Jour. Iron and Steel Institute*, 1893, 153.

mortar to the required degree of fineness, a little water being added to facilitate the grinding.

(2) The water solution of the melt, before acidulation, must be freed from an excess of sodium peroxide. Whenever sodium ferrate or sodium manganate is formed during the fusion it must be decomposed in the water solution of the melt.

(3) As the result of the analysis depends to a large extent upon the titration, and especially upon a clear perception of its final point, it is important that the solution in which the chrome is to be determined should be as free as possible from other metallic salts, as for instance, iron, manganese, and nickel salts. We have also observed that the ferricyanide solution which is used as an indicator is most satisfactory when it contains no more than 1 per cent. of ferricyanide.

Iodimetric Determination of Chromic Acid.—H. P. Seubert and Henke* have devised a method which depends upon the reaction :

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

Under ordinary circumstances the action takes considerable time. The authors have made an exhaustive investigation of its rate of progress when the different bodies are present in different quantities. Increasing the proportion of acid accelerates the reaction more than increasing the proportion of potassium iodide does ; dilution greatly retards it. The following are convenient proportions to use : Dichromate, 0·05 gm. ; potassium iodide, 0·5 gm. ; sulphuric acid, 1·8 gm. ; total volume, 100 c.c. If less than 0·05 gm. of dichromate be present, the other quantities should still be kept the same. If there be more dichromate, the iodide and acid should be proportionately increased without adding more water, unless there be more than 0·25 gm. The reaction is complete in about six minutes. The liquid should then be diluted and titrated with thiosulphate solution, using starch as indicator.

COBALT.

Co = 58·97.

Determination by Permanganate and Mercuric Oxide (C. Winkler).

The volumetric determination of cobalt, especially in the presence of other metals, is not yet very satisfactory. The method here mentioned is worthy of notice, and with an alteration suggested by H. B. Harris† is capable of giving fair technical results. This alteration consists in carrying out the titration in a hot solution instead of a cold one, as appears to have been done by Winkler. If an aqueous solution of cobaltous chloride or sulphate be treated with an emulsion of precipitated mercuric oxide, no decomposition ensues ; but on the addition of permanganate to the mixture, hydrated cobaltic and manganic oxides are precipitated, and the

* *Zeit. f. ang. C.*, 1900, 1147.

† *J. Am. C. S.*, 1898, 173.

mercuric oxide is simply used to mechanically separate the resulting oxides. It is probable that no definite equation can be given for the reaction, and therefore practically the working effect of the permanganate is best determined by a standard solution of cobalt of known strength, say metallic cobalt dissolved as chloride, or neutral cobaltous sulphate.

METHOD OF PROCEDURE: The solution of about 0·1 to 0·2 gm. of the metal, free from any great excess of acid is placed in a flask, diluted to about 200 c.c., and a tolerable quantity of mercuric emulsion (precipitated from the nitrate or perchlorate by alkali and washed) added. Permanganate from a burette is then slowly added to the hot solution with constant shaking until the rose colour appears in the clear liquid above the bulky brownish precipitate.

The appearance of the mixture is somewhat puzzling at the beginning, but as more permanganate is added the precipitate settles more freely, and the end as it approaches is very easily distinguished. The process is complete when the rose colour is persistent for a minute or two; subsequent bleaching must not be regarded.

The actual decomposition as between cobaltous chloride and permanganate may be formulated thus—

$$6CoCl_2 + 5HgO + K_2Mn_2O_8 + H_2O = 3Co_2(OH)_6 + 5HgCl_2 \\ + 2KCl + 2MnO_2H_2O$$

but as this exact decomposition cannot be depended upon to take place in all mixtures, it is not possible to accept systematic numbers calculated from normal solutions.

Solutions containing manganese, phosphorus, arsenic, active chlorine, oxygen compounds, or organic matter, cannot be used in this method of determination; moderate quantities of copper or lead are of no consequence. Nor is antimony when its quantity is double or more than the cobalt, but if less the results are too high.

A further modification of this method was advocated by von Reis and Wiggert, and possesses the advantage of being easy and simple in execution. Very fair results were obtained by H. B. Harris on trial at the same time as the examination of Winkler's method.

METHOD OF PROCEDURE: The solution of cobalt is mixed with an emulsion of zinc oxide and heated to boiling. A standard solution of permanganate is then added in known quantity, but more than enough to precipitate the oxidized cobalt. The latter precipitate settles to the bottom, the excess of permanganate is then found by titration with a standard solution of ferrous ammonium sulphate.

R. L. Taylor* has experimented on Rose's method of separating cobalt from nickel, and has improved it by using a perfectly neutral solution instead of a strongly acid one as used by Rose; the latter neutralized the solution by calcium or barium carbonate, but the CO_2 so produced retarded or altogether stopped the precipitation of the cobalt oxide. By the new process the result is that a dilute neutral solution of cobalt may be quantitatively precipitated by barium or calcium carbonate in presence of bromine water. If the liquid from which the cobalt is to be precipitated is acid, the acid must be neutralized by an excess of carbonate and well boiled to expel all the CO_2, and then cooled

* *C. N.* **88**, 184.

before the bromine water is added. Not only CO_2 but zinc also stops the precipitation.

The composition of the black oxide is not quite clear, but it is fairly constant in composition, and if dissolved with HCl and KI the amount is ascertained by titrating the liberated iodine. The method has been tested by J. H. Davidson in the assay of cobalt ores, and he finds it much more rapid than the usual methods and sufficiently accurate for assay purposes.

For other methods for the determination of Cobalt, see under Nickel.

COPPER.

$Cu = 63·57.$

1 c.c. $^N/_{10}$ solution $= 0·006357$ gm. Cu.
Iron $\times 1·138 = $ Cu.
Double Iron Salt $\times 0·1622 = $ Cu.

1. Reduction by Grape Sugar and subsequent titration with Ferric Chloride and Permanganate (Schwarz).

THIS process is based upon the fact that grape sugar precipitates cuprous oxide from an alkaline solution of the metal containing tartaric acid; the oxide so obtained is collected and mixed with ferric chloride and hydrochloric acid. The result is the following decomposition :—

$$Cu_2O + Fe_2Cl_6 + 2HCl = 2CuCl_2 + 2FeCl_2 + H_2O.$$

Each equivalent of copper reduces one equivalent of ferric to ferrous chloride, which is determined by permanganate with due precaution. The iron so obtained is calculated into copper by the requisite factor.

METHOD OF PROCEDURE: The weighed substance is brought into solution by nitric or sulphuric acid or water, in a porcelain dish or glass flask, and most of the acid in excess neutralized with sodium carbonate; neutral potassium tartrate is then added in not too large quantity, and the precipitate so produced dissolved to a clear blue liquid by adding caustic potash or soda in excess; the vessel is next heated cautiously to about 50° C. in the water bath, and sufficient grape sugar added to precipitate the copper present; the heating is continued until the precipitate is of a bright red colour, and the upper liquid is brownish at the edges from the action of the alkali on the sugar; the temperature must never exceed 90° C. When the mixture has somewhat cleared, the upper fluid is poured through a moistened filter, and afterwards the precipitate brought on the same, and washed with hot water till thoroughly clean; the precipitate which may adhere to the dish or flask is well washed, and the filter containing the bulk of the protoxide put with it, and an excess of solution of ferric chloride (free from nitric acid or free chlorine) added, together with a little sulphuric acid; the whole is then warmed and stirred until the cuprous chloride is all dissolved. It is then filtered into a good-sized flask, the old and new filters being well washed with hot water, to which at first a little free sulphuric acid should be added, in order to be certain of dissolving all the oxide in the folds of the paper. The entire solution is then titrated with permanganate in the usual way. Dichromate may also be used, but the end of the reaction is not so distinct as usual, from the turbidity produced by the presence of copper.

A modification of this permanganate method, which gives very

good technical results, has been devised by R. K. Meade,* in which the copper is precipitated as thiocyanate. The author considers it superior in accuracy to the iodide method; but with this I cannot agree, except in certain cases.

METHOD OF PROCEDURE: The copper is brought into solution as a sulphate, either by dissolving it in sulphuric acid or by evaporation of its solution with sulphuric acid. The greater part of the free acid is neutralized by ammonia, the solution warmed, sulphurous acid added until the solution smells strongly of the reagent, and then a slight excess of ammonium or potassium thiocyanate. The copper is immediately precipitated as cuprous thiocyanate. Stirring and warming renders the precipitate heavy and easily handled. The solution is filtered through asbestos, using the pump, and well washed. The precipitate and filter are thrown into the beaker in which the precipitation was made and heated with a solution of caustic soda or caustic potash. Double decomposition takes place. Hydrated cuprous oxide and potassium or sodium thiocyanate result—

$$2CuSCN + 2KOH = Cu_2(OH)_2 + 2KSCN.$$

The oxide is filtered on asbestos and washed well with hot water. The precipitate and filter are again placed in the same beaker and an excess of ferric chloride or ferric sulphate (free from nitric acid, free chlorine, or ferrous salts), together with a little dilute sulphuric acid, added. The copper oxide reduces a corresponding amount of iron from the ferric to the ferrous condition—

$$Cu_2O + Fe_2Cl_6 + 2HCl = 2CuCl_2 + 2FeCl_2 + H_2O.$$

The beaker is warmed and stirred until all the copper oxide is dissolved. The solution is then poured through a perforated platinum disc, and the asbestos which remains behind upon it washed with water, to which has been added a little sulphuric acid and a little ferric chloride or sulphate. The solution is then titrated with permanganate. The iron equivalent to the permanganate used multiplied by 1·138 gives the weight of copper in the sample.

Instead of sulphurous acid, ammonium or sodium bisulphite may be used to reduce the copper. A solution of equal weights of sodium bisulphite and potassium thiocyanate answers well as a reagent for the precipitation of the metal. Since copper is the only metal precipitated by an alkali thiocyanate from an acid solution, the presence of arsenic, antimony, bismuth, zinc, and other elements which render the electrolytic, the cyanide, and the iodine methods inaccurate will not affect the results.

The caustic alkali solution, used to convert the cuprous thiocyanate into cuprous hydroxide, must not be too strong, or some of the metal will go into solution, colouring the liquid blue. About a half normal solution of caustic potash, made by dissolving 28 gm. of the salt in a litre of water, is a convenient strength. Either ferric sulphate or ferric chloride may be used to dissolve the cuprous oxide. The former is probably the safer, but the latter appears to dissolve the precipitate the more readily of the two.

2. Reduction by Zinc and subsequent titration with Ferric Chloride and Permanganate (Fleitmann).

The metallic solution, free from nitric acid, bismuth, and lead, is precipitated with clean sticks of pure zinc; the copper collected, washed, and dissolved in a mixture of ferric chloride and hydrochloric acid; a little sodium carbonate may be added to expel the atmospheric air. The reaction is—

$$Cu + Fe_2Cl_6 = CuCl_2 + 2FeCl_2.$$

* *J. Am. C. S.* **20**, 610.

When the copper is all dissolved, the solution is diluted and titrated with permanganate ; 55·85 Fe = 31·79 Cu, or 1 Fe = ·5692 Cu.

If the original solution contains nitric acid, bismuth, or lead, the decomposition by zinc must take place in an ammoniacal solution, from which the precipitates of either of the above metals have been removed by filtration ; the zinc must in this case be finely divided and the mixture warmed. The copper is all precipitated when the colour of the solution has disappeared. It is washed first with hot water, then with weak HCl and water to remove the zinc, again with water, and then dissolved in the acid and ferric chloride as before.

3. Determination as Cuprous Iodide.

This excellent method is based on the fact that when potassium iodide is mixed with a salt of copper in acid solution cuprous iodide is precipitated as a dirty white powder and iodine set free. If the latter is then immediately titrated with thiosulphate and starch, the corresponding quantity of copper is found.

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

The solution of the metal, if it contain nitric acid, is evaporated with sulphuric acid till the former is expelled, or the nitric acid is neutralized with sodium carbonate, and acetic acid added ; the sulphate solution must be neutral, or only faintly acid ; excess of acetic acid is of no consequence, and therefore it is always necessary to get rid of all free mineral acids and work only with free acetic acid.

J. W. Westmoreland,* who has had very large experience in examining a variety of copper products, and has worked the process in my own laboratory, strongly recommends it for the determination of copper in its various ores, etc. The metal may very conveniently be separated from a hot sulphuric acid solution by sodium thiosulphate : this gives a flocculent precipitate of subsulphide mixed with sulphur, which filters readily, and can be washed with hot water. Arsenic and antimony, if present, are also precipitated ; tin, zinc, iron, nickel, cobalt, and manganese are not precipitated. On igniting the precipitate most of the arsenic and the excess of sulphur are expelled, an impure subsulphide of copper being left. Sulphuretted hydrogen may of course be used instead of the thiosulphate, but its use is objectionable to many operators ; moreover, in some circumstances, a small amount of copper remains in the solution, and iron in small quantity is also precipitated with the copper and cannot be entirely removed by washing. If H_2S is used it should be passed for some time, and the precipitate allowed to stand a few hours to settle ; after filtration and washing the CuS should be redissolved in HNO_3 and reprecipitated with the gas, it is then quite free from iron.

* *J. S. C. I.*, **5**, 51.

Standardizing the Thiosulphate Solution.—This may be done on pure electrotype copper, but this is not always to be had pure, and the safest standard is high conductivity wire, first dissolving in nitric acid, boiling to expel nitrous fumes, diluting, neutralizing with sodium carbonate till a precipitate appears, then adding acetic acid till clear. The liquid is then made up to a definite volume, and a quantity equal to about 0·5 gm. Cu taken in a flask or beaker, about ten times the copper weight of potassium iodide added, and when dissolved the thiosulphate is run in from a burette until the free iodine is nearly removed, some starch then added, and the titration finished in the usual way. The thiosulphate will of course need to be checked occasionally.

If strictly $^{N}/_{10}$ thiosulphate is used, each c.c. = 0·006357 gm. Cu.

METHOD OF PROCEDURE: For determining the copper in iron pyrites or burnt ore 5 gm. of the substance should be taken, 2 gm. for 30-40 % mattes or 1 gm. for 60 % mattes, and with precipitates it is best to dissolve say 5 gm. and dilute to a definite volume, and take as much as would represent from 0·5 to 0·7 gm. of Cu for titration. The solution is made with nitric acid, to which hydrochloric is also added later on, and then evaporated to dryness with excess of sulphuric acid to convert the bases into sulphates; the residue is treated with warm water and any insoluble $PbSO_4$, etc., filtered off. The filtrate is heated to boiling and precipitated with thiosulphate, this precipitate is filtered off, washed with hot water, dried, and roasted; the resulting copper oxide is then dissolved in nitric acid, and after the excess of acid has been mainly removed by evaporation, sodium carbonate is added so as to precipitate part of the copper and ensure freedom from mineral acid, acetic acid is added till a clear solution is obtained; about ten parts of potassium iodide to one of copper supposed to be present are then added, and the titration carried out in the usual way.

An excellent modification of this method, much used in America, is described by A. H. Low.* A solution of thiosulphate is used containing about 19 gm. per litre, which is standardized upon about 0·2 gm. of pure copper foil dissolved in 5 or 6 c.c. of nitric acid sp. gr. 1·2 in a 250 c.c. flask in the following manner:—

Heat the nitric acid solution to boiling, add 5 c.c. strong bromine water, and again boil till all nitrous fumes and bromine are expelled. As soon as the incrusted matter has dissolved, add a slight excess of ammonia, boil off the excess, then add 3 to 4 c.c. of acetic acid, which dissolves any precipitated copper hydroxide (boiling again may be necessary), after cooling and diluting to about 50 c.c. add 3 gm. of KI and titrate with thiosulphate as usual.

METHOD OF PROCEDURE FOR ORES: Treat 0·25-0·5 gm. of finely ground ore with 5 or 6 c.c. of nitric acid 1·42 sp. gr. and evaporate nearly to dryness. Dissolve all incrusted matter by heating with 5 c.c. strong hydrochloric acid, add 7 c.c. sulphuric acid and heat, to expel volatile acids, till the sulphuric acid fumes freely. After cooling and diluting with 25 c.c. of water, heat to dissolve any anhydrous ferric sulphate, and filter. The filtrate and washings, which should not much exceed 75 c.c., are received in a small beaker. The copper is now precipitated by means of aluminium as follows:—Place in the beaker two pieces of stout sheet aluminium, about one-sixteenth of an inch in thickness, which, for the sake of convenience in subsequent washing, should be 1½ inch square with the four corners bent, for about a quarter of an inch, alternatively up and down at right angles. This prevents the pieces from lying flat against each other or upon the bottom of the beaker. The same pieces may be used repeatedly,

* *J. Am. C. S.* **18**, 458, and **24**, 1082.

as they are but little attacked each time. Cover the beaker and boil gently for 7-10 minutes. Unless the bulk of the solution is excessive, this will be quite sufficient for all percentages of copper. Ordinarily the aluminium will be found to be clean, and nearly or quite free from precipitated copper. If, by chance, the copper adheres to any considerable extent, it will usually become loosened by a little additional boiling, or it may be removed by the aid of a glass rod. Rinse the cover and sides of the beaker with cold water. To prevent oxidation of finely-divided copper during subsequent washing and at the same time to remove any traces of copper still in solution, add about 15 c.c. strong H_2S water. Transfer the solution back to the original flask, and by means of a jet of H_2S water from a wash-bottle rinse in also as much of the copper as possible, leaving the aluminium behind. Drain the beaker as completely as possible, and temporarily set aside with the aluminium, which may still retain a little copper. Allow the copper in the flask to settle, and then decant the liquid through a filter. Again wash the copper similarly two or three times with about 20 c.c. H_2S water each time, retaining it as completely as possible in the flask. Finally, wash the filter once or twice and endeavour to rinse all metallic particles down into the point. Now pour upon the aluminium in the beaker 5 c.c. of nitric acid* 1·2 sp. gr., and warm the beaker gently, but do not heat to boiling, as the aluminium would be thereby unnecessarily attacked. See that any copper present is dissolved, and pour the hot solution very slowly through the filter, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main portion of the copper. Before washing the filter pour upon it 5 c.c. of bromine water, and wash the filter and beaker with hot water. The bromine must be in sufficient excess to give a slight tinge to the filtrate. Boil the filtrate to remove bromine, add excess of ammonia, and proceed as described above for copper foil in standardizing. If the percentage of Cu in the ore does not exceed 20 per cent., the precipitated metal may be washed with H_2S water upon the filter, instead of by decantation, care being taken that the filter is kept filled till the washing is complete, to avoid oxidation.

A. M. Fairlie† uses ammonium thiocyanate, in preference to sodium thiosulphate or aluminium, to separate the copper.

The cuprous thiocyanate is dissolved in strong nitric acid, the solution boiled till red fumes are no longer evolved, then neutralized with ammonia, acidified with acetic acid, KI added and the titration carried out in the usual way. The presence of much ammonium acetate must be avoided.

4. Determination by Potassium Cyanide (Parkes and C. Mohr).

(A solution containing 40 grams potassium cyanide per litre is used) 1 c.c. = (about) ·01 gm. copper.

This well-known and much-used process for determining copper depends upon the decoloration of an ammoniacal solution of copper by potassium cyanide. The reaction (which is not absolutely uniform with variable quantities of ammonia) is such that a double cyanide of copper and ammonia is formed; cyanogen is also liberated, which reacts on the free ammonia, producing urea, oxalate of urea, ammonic cyanide and formate (Liebig). Owing to the influence

* Videgren (*Z. a. C.*, 1909, 539) prefers to dissolve in a mixture of potassium chlorate and hydrochloric and sulphuric acids. If arsenic or antimony are present, sodium acetate is added before titrating. The end-points obtained are said to be much sharper than with Low's method of solution.

† *Eng. and Mining J.*, 1904, 787.

exercised by variable quantities of ammonia, or its neutral salts, upon the decoloration of a copper solution by the cyanide, it has been suggested by Beringer to substitute some other alkali for ammonia in neutralizing the free acid in the copper solution. The suggestion has been adopted by Davies* and by Fessenden† who both recommend sodium carbonate. My own experiments completely confirm their statement that none of the irregularities observed with variable quantities of ammonia or its salts occur with soda or potash. Suppose, for example, that copper has been separated as sulphide, and brought into solution by nitric acid, the free acid is neutralized with Na_2CO_3, and an excess of it added to redissolve the precipitate. The cyanide solution is then cautiously run into the light blue solution until the colour is just discharged. My own experience is that it is impossible to redissolve the whole of the precipitate without using a very large excess of soda; but there is no need to add such an excess, as the precipitate easily dissolves when the cyanide is added. I have used a modification of this method which gives excellent results, viz., to neutralize the acid copper solution either with Na_2CO_3 or NaHO, add a trifling excess, and then 1 c.c. of ammonia 0·960 sp. gr.; a deep blue clear solution is at once given, which permits of very sharp end-reaction with the cyanide.

J. J. and C. Beringer‡ have already adopted the method of neutralizing the acid copper solution with soda, then adding ammonia, but the proportion they recommend is larger than necessary.

In standardizing the cyanide, it is advisable so to arrange matters that copper is precipitated with soda exactly as in the titration of a copper ore; that is to say, free nitric or nitro-sulphuric acid should be added, then neutralized with slight excess of soda, cleared with 1 c.c. of ammonia, then titrated with cyanide. Large quantities of nitrate or sulphate of soda or potash, however, make very little difference in the quantity of cyanide used.

It has generally been thought that where copper and iron occur together, it is necessary to separate the latter before using the cyanide. F. Field,‖ however, has stated that this is not necessary; and I can fully endorse his statement that the presence of the suspended ferric oxide is no hindrance to the determination of the copper; in fact, it is rather an advantage, as it acts as an indicator to the end of the process.

While the copper is in excess, the oxide possesses a purplish-brown colour, but as this excess lessens, the colour becomes gradually lighter, until it is orange brown. If it be now allowed to settle, which it does very rapidly, the clear liquid above will be found nearly colourless. A little practice is of course necessary to enable the operator to hit the exact point.

It is impossible to separate the ferric oxide by filtration without leaving some copper in it, and no amount of washing will remove it. For example, 10 c.c. of a copper solution with 10 c.c. of ferric

* *C. N.* **58**, 131. † *C. N.* **61**, 131. See also Fernekes and Koch, *J. A. C. S.*, **27**, 1224.
‡ *C. N.* **49**, 3. ‖ *C. N.* **1**, 25.

solution were directly titrated with cyanide after treatment with NaHO in slight excess and 1 c.c. of ammonia. The cyanide required was 12 c.c. Another 10 c.c. of the same copper and iron solutions were then precipitated with soda and ammonia in same proportions. This gave a complete solution of the copper with the ferric oxide suspended in it. The solution was filtered and the ferric oxide well washed with hot water, then the filtrate cooled and titrated with cyanide, 9·5 c.c. only being required. On treating the ferric oxide on the filter with nitric acid, neutralizing with NaHO and NH_3 in proper proportions exactly, 2·5 c.c. of cyanide were required, showing that the ferric oxide had retained 20 per cent. of the copper.

I strongly recommend that operators who have to deal with copper determination in samples containing much iron should practise the use of the cyanide method in the presence of the iron, and accustom their eyes to the exact colour which the ferric oxide takes when the titration is finished, always, however, with this proviso, that the cyanide solution is standardized upon a known weight of copper in the presence of a moderate amount of iron.

The solution of potassium cyanide should be titrated afresh at intervals of a few days. Further details of this process are given on p. 201 (8).

Dulin* advocates the cyanide process for copper ores as follows :

METHOD OF PROCEDURE : The ore is treated in the way described on p. 194 to obtain a solution of the copper practically free from silver and lead. The copper is then precipitated upon aluminium foil as there mentioned. Should cadmium be present it is also precipitated to some extent, but only after the copper is thrown down. If care be taken to stop the boiling immediately after the copper is precipitated, which a practised eye will readily detect, the amount of cadmium precipitated is so small as to cause no sensible error. The liquid being decanted from the copper and foil, the latter are washed well with hot water, taking care to lose no metal ; when quite clean, dilute nitric acid is added and boiled till the copper is dissolved, the liquid then neutralized with excess of ammonia, and titrated with cyanide in the usual way.

5. Determination as Sulphide (Pelouze).

It is first necessary to have a solution of pure copper of known strength, which is best made by dissolving 39·286 gm. of pure re-crystallized cupric sulphate in 1 litre of water ; each c.c. will contain 0·01 gm. Cu.

Precipitation in Alkaline Solution.—This process is based on the fact that if an ammoniacal solution of copper is heated to from 40° to 80° C., and a solution of sodium sulphide added, the whole of the copper is precipitated as oxysulphide, leaving the liquid colourless. The loss of colour indicates, therefore, the end of the process, and this is its weak point. Special practice, however, will enable the operator to hit the exact point closely.

Casamajor† uses instead of ammonia the alkaline tartrate

* *Jour. Amer. Chem. Soc.* **17**, 346. † *C. N.* **45**, 167.

solution of Fehling, adding a slight excess so as to make a clear blue solution. The addition of the sulphide gives an intense black brown precipitate, the liquid being stirred vigorously till clear. The copper sulphide agglomerates into curds, and the reagent is added until no further action occurs with a drop of the sodium sulphide. This modification can also be used for lead. $PbSO_4$ is easily soluble in the tartrate solution, and can be determined by the sodium sulphide in the same way as copper.

The colour of the solution is not regarded, but the clotty precipitate of sulphide, which is easily made to agglomerate by vigorous stirring. Very good results may be gained by this modification.

Copper can also be first separated by glucose, or as thiocyanate (Rivot), then dissolved in HNO_3, and treated with the tartrate.

Precipitation in Acid Solution.—The copper solution is placed in a stoppered flask (400 or 500 c.c.), freely acidified with hydrochloric acid, then diluted with about 200 c.c. of hot water.

The alkali sulphide is then delivered in from a burette, the stopper replaced, and the mixture well shaken; the precipitate of copper sulphide settles readily, leaving the supernatant liquid clear; fresh sulphide solution is then added at intervals until no more precipitate is produced. The calculation is the same as in the case of alkaline precipitation, but the copper is precipitated as sulphide instead of oxysulphide.

6. Determination by Stannous Chloride (Weil).*

This process is based on the fact that a solution of a cupric salt in large excess of hydrochloric acid at a boiling heat shows, even when the smallest trace is present, a greenish-yellow colour. If to such a solution stannous chloride is added in minute excess, a colourless cuprous chloride is produced, and the loss of colour indicates the end of the process.

$$2CuCl_2 + SnCl_2 = Cu_2Cl_2 + SnCl_4.$$

The change is easily distinguishable by the eye, but should any doubt exist as to whether stannous chloride is in excess, a small portion of the solution may be tested with mercuric chloride. Any precipitate of calomel indicates the presence of stannous chloride.

The tin solution is prepared as described on p. 128.

A standard copper solution is made by dissolving pure copper sulphate in distilled water, in the proportion of 39·286 gm. per litre = 10 gm. of Cu.

Method of Procedure for Copper alone.—10 c.c. of the copper solution (= 0·1 gm. of Cu) are put into a white-glass flask, 25 c.c. of pure strong hydrochloric acid added, placed on a sand-bath and brought to boiling heat; the tin solution is then quickly delivered in from a burette until the colour is nearly destroyed, finally a drop at a time till the liquid is as colourless as distilled water. No oxidation will take place during the boiling, owing to the flask being filled with acid vapours.

* *Z. Anal. Chem.* **9**, 297.

A sample of copper ore is prepared in the usual way by treatment with nitric acid, which is afterwards removed by evaporating with sulphuric acid. Silica, lead, tin, silver, or arsenic, are of no consequence, as when the solution is diluted with water to a definite volume, the precipitates of these substances settle to the bottom of the measuring flask, and the clear liquid may be taken out for titration. In case antimonic acid is present it will be reduced with the copper, but on exposing the liquid for a night in an open basin, the copper will be completely re-oxidized but not the antimony; a second titration will then show the amount of copper.

Method of Procedure for Ores containing Copper and Iron.—In the case of copper ores where iron is also present, the quantity of tin solution required will of course represent both the iron and the copper. In this case a second titration of the original solution is made with zinc and permanganate, and the quantity so found is deducted from the total quantity; the amount of tin solution corresponding to copper is thus found.

EXAMPLE: A solution was prepared from 10 gm. of ore and diluted to 250 c.c.; 10 c.c. required 26·75 c.c. of tin solution whose strength was 16·2 c.c. for 0·1 gm. of Cu.

10 c.c. of ore solution were diluted, zinc and platinum added, warmed till reduction was complete, and the solution titrated with permanganate, of which the quantity used $=0{\cdot}0809$ gm. of Fe.

The relative strength of the tin solution to iron is found thus:—

$$\begin{aligned} 63{\cdot}57 : 0{\cdot}1 &= 55{\cdot}85 : x \\ x &= {\cdot}0879 \\ \text{i.e., } 0{\cdot}1 \text{ gram Cu} &= {\cdot}0879 \text{ gram Fe.} \\ &= 16{\cdot}2 \text{ c.c. } SnCl_2. \end{aligned}$$

Again,

$$\begin{aligned} {\cdot}0879 : {\cdot}0809 &= 16{\cdot}2 : y \\ y &= 14{\cdot}9 \\ \text{i.e., } 0{\cdot}0809 \text{ Fe found above} &= 14{\cdot}9 \text{ c.c. } SnCl_2 \\ \text{Hence, iron + copper} &= 26{\cdot}75 \text{ c.c. } SnCl_2 \\ \text{Iron} &= 14{\cdot}9 \\ \hline \text{Copper} &\quad 11{\cdot}85 \end{aligned}$$

Finally,

$$\begin{aligned} 16{\cdot}2 : 11{\cdot}85 &= 0{\cdot}1 : z \\ z &= 0{\cdot}07315. \end{aligned}$$

That is, 10 c.c. of ore solution contain 0·07315 gram Cu, or 250 c.c. (=10 grams of ore) contain $\cdot07315 \times \frac{100}{4} = 1{\cdot}829$ gm.

The percentage of copper is, therefore, 18·29.

A gravimetric determination as a control gave 18·34 per cent. Cu.

Fe determined volumetrically gave 20·25 %, gravimetrically 20·10 %.

The method is specially adapted for the technical analysis of fahl-ores.

7. Precipitation as Cuprous Thiocyanate, Volhard's method.

The necessary standard solutions are described on p. 145. Each c.c. of $^{N}/_{10}$ thiocyanate represents 0·006357 gm. Cu.

$$2CuSO_4 + 2KSCN + SO_2 + 2H_2O = 2CuSCN + 2H_2SO_4 + K_2SO_4.$$

METHOD OF PROCEDURE: The copper in sulphuric or nitric acid solution is evaporated to remove excess of acid, or if the acid is small in quantity neutralized with sodium carbonate, washed into a 500 c.c. flask, and enough aqueous solution

of SO_2 added to dissolve the traces of basic carbonate and leave a distinct smell of SO_2. Heat to boiling, and run in the thiocyanate from a burette until the addition produces no change of colour, add 3 or 4 c.c. more, and note the entire quantity used, allow to cool, fill to mark, and shake well. 100 c.c. are then filtered through a dry filter, 10 c.c. of ferric indicator with some nitric acid added, then titrated with $^N/_{10}$ silver nitrate till colourless: then again thiocyanate till the reddish colour appears. The volume of silver solution, less the final correction with thiocyanate, deducted from the original thiocyanate, will give the volume of the latter required to precipitate the copper.

The process is not accurate in presence of Fe, Ag, Hg, Cl, I, Br, or As_2O_5.

Several modern processes for the volumetric determination of copper, chiefly due to American chemists, have been based upon the separation of the metal as cuprous thiocyanate. One (Fairlie's) has already been mentioned as a modification of the iodide method. In another (Meade's, see p. 192), the iron equivalent of the separated copper is titrated with permanganate. In all cases the precipitation as thiocyanate is effected as already described.

GARRIGUE'S ACIDIMETRIC METHOD.* The washed thiocyanate precipitate, with the filter, is decomposed by boiling with caustic alkali (see Meade's method, p. 192), excess of normal soda being used, and the excess, after filtering off the cuprous hydroxide, titrated by normal acid, with methyl orange as indicator. The method is said to be especially useful in alloy assay.

PARR'S PERMANGANATE METHOD.† The precipitated cuprous thiocyanate is decomposed by caustic alkali, the copper oxidized in alkaline solution by permanganate without decomposition of the alkali thiocyanate, and the thiocyanic acid titrated in acid solution with permanganate, the whole being effected in one operation as follows:—The washed precipitate of cuprous thiocyanate and the asbestos pulp or filter paper are treated with 10 c.c. of a 10 % solution of caustic potash and 10 c.c. of ammonia (sp. gr. 0·96), and then immediately titrated with permanganate until, upon warming to about 50° C., the green colour of the supernatant liquid remains. About one-third or one-fourth of the quantity of permanganate necessary for this is then run in, the mixture allowed to stand for 5 minutes, then acidified with 25 c.c. sulphuric acid (1 : 1 or 2) and titrated to a pink colouration with permanganate. 10 atoms of cuprous Cu are oxidized by 7 molecules of permanganate. The copper value of the latter is found by multiplying the iron factor by 0·1602.

IODATE METHOD.‡ The application of the potassium iodate method of Andrews (p. 132) has been found to afford a simple and accurate process for the titration of cuprous thiocyanate. The washed precipitate, together with the asbestos or filter-paper on which it was filtered, is placed in a bottle, 5 c.c. of chloroform, 20 c.c. of water, and 30 c.c. of hydrochloric acid are added, and a standard solution of potassium iodate, containing 11·784 grams of the salt per litre, is run in with constant shaking, until the colour first formed in the chloroform disappears. The reaction proceeds according to the equation:

$$4CuSCN + 7KIO_3 + 14HCl = 4CuSO_4 + 7KCl + 7ICl + 4HCN + 5H_2O.$$

One c.c. of the standard solution corresponds to 0·0020 gram of copper. The chloroform may be used a second time.

To apply the method to *ores*, the sample is dissolved in nitric acid or aqua regia, and boiled down with sulphuric acid until fumes of the latter are given off. The residue is diluted and filtered after the addition of 1 or 2 drops of hydrochloric

* *J. A. C. S.*, **19**, 940.

† *J. A. C. S.* **22**, 685 and **24**, 580. See also Hawley, *Eng. and Mining J.* 1908, 1155, and *J. S. C. I.*, 1909, 163.

‡ Jamieson, Levy, and Wells, *J. A. C. S.*, 1908, 760.

acid if silver is present. The small quantities of lead and antimony left in solution do not interfere with the subsequent precipitation of the copper by means of sulphur dioxide and ammonium thiocyanate. A complete determination can be made in one hour.

Potassium iodate can be obtained pure, and its solution is very stable.

8. Technical Examination of Copper Ores (Steinbeck's Process).

In 1867 the Directors of the Mansfield Copper Mines offered a premium for the best method of examining these ores, the chief conditions being tolerable accuracy, simplicity of working, and the possibility of one operator making at least eighteen assays in the day.

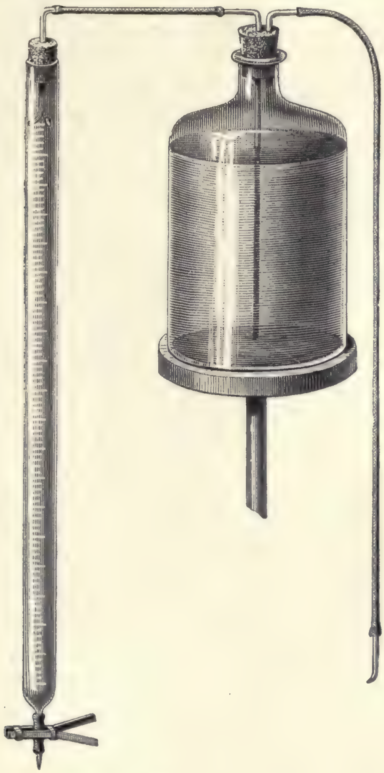


Fig. 42.

The fortunate competitor was Dr. Steinbeck, whose process completely satisfied the requirements. The whole report is contained in *Z. a. C.* viii. 1, and is also translated in *C. N.* xix. 181. The following is a condensed account of the process, the final titration of the copper being accomplished by potassium cyanide as on p. 195.

A very convenient arrangement for filling the burette with standard solution where a series of analyses has to be made, and the burette continually emptied, is shown in fig. 42; it may be refilled by simply blowing upon the surface of the liquid.

(*a*) **The extraction of the Copper from the Ore.**—5 gm. of pulverized ore are put into a flask with from 40 to 50 c.c. of hydrochloric acid (specific gravity 1·16), whereby all carbonates are converted into chlorides, while carbonic acid is expelled.

After a while there is added to the fluid in the flask 6 c.c. of a special nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1·42 sp. gr. As regards certain ores, however, specially met with in the district of Mansfield, some, having a very high percentage of sulphur and bitumen, have to be roasted previous to being subjected to this process; and others, again, require only 1 c.c. of nitric acid instead of 6. The flask containing the assay is digested on a sand-bath for half an hour, and the contents boiled for about fifteen minutes; after which the whole of the copper occurring in the ore, and all other metals, are in solution as chlorides. The blackish residue, consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or to contain at the most only 0·01 to 0·03 per cent.

(*b*) **Separation of the Copper.**—The solution of metallic and alkaline earthy chlorides, and some free HCl, obtained as just described, is separated by filtration from the insoluble residue, and the fluid run into a covered beaker of about 400 c.c. capacity. In this beaker a rod of metallic zinc, weighing about 50 gm., has been previously placed, fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as free as possible from lead, and at any rate should not contain more than from 0·1 to 0·3 per cent. of the latter metal. The precipitation of the copper in the metallic state sets in during the filtration of the warm and concentrated fluid, and is, owing especially also to the entire absence of nitric acid, completely finished in from half to three-quarters of an hour after the beginning of the filtration. If the fluid be tested with SH_2 no trace of copper can or should be detected; the spongy metal partly covers the platinum foil, partly floats about in the liquid, and in case either the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitated copper. After the excess of zinc (for an excess must always be employed) has been removed, the metal is repeatedly and carefully washed by decantation with fresh water, and care taken to collect together every particle of the spongy mass.

(*c*) **Determination of the precipitated Copper.**—To the spongy metallic mass in the beaker, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the special nitric acid are added, and the copper dissolved by the aid of moderate heat in the form of cupric nitrate, which, in the event of any small quantity of lead being present, will of course be contaminated with lead.

When copper ores are dealt with containing above 6 per cent. of copper, which may be approximately determined from the bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are applied for dissolving the metal. The solution thus obtained is left to cool, and next mixed, immediately before titration with cyanide, with 10 c.c. of special solution of liquid ammonia, prepared by diluting 1 volume of liquid ammonia (sp. gr. 0·93) with 2 volumes of distilled water.

The titration with cyanide is conducted as described on p. 195.

In the case of such ores as yield over 6 per cent. of copper, and when a double quantity of nitric acid has consequently been used, the solution is diluted with water, and made to occupy a bulk of 100 c.c.; this bulk is then exactly divided into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of ammonia, and the copper therein volumetrically determined. The deep blue coloured solution only contains, in addition to the copper compound, ammonium nitrate; any lead which might have been dissolved having been precipitated as hydrated oxide, which does not interfere with the titration with cyanide. The solution of the last-named salt is so arranged that 1 c.c. thereof indicates exactly

0·005 gm. of copper (about 21 gm. of the pure salt per litre). Since, for every assay, 5 gm. of ore have been taken, 1 c.c. of the titration fluid is equal to 0·1 per cent. of copper, it hence follows that, by multiplying the number of c.c. of cyanide solution used to make the blue colour of the copper solution disappear by 0·1, the percentage of copper contained in the ore is immediately ascertained.

Steinbeck tested this method specially, in order to see what influence is exercised thereupon by (1) ammonium nitrate, (2) caustic ammonia, (3) lead. The copper used for the experiments for this purpose was pure metal, obtained by galvanic action, and was ignited to destroy any organic matter which might accidentally adhere to it, and next cleaned by placing it in dilute nitric acid. 5 gm. of this metal were placed in a litre flask, and dissolved in 266·6 c.c. of special nitric acid, the flask gently heated, and, after cooling, the contents diluted with water, and thus brought to a bulk of 1000 c.c. 30 c.c. of this solution were always applied to titrate one and the same solution of cyanide under all circumstances. When 5 gm. of ore, containing on an average 3 per cent. of copper, are taken for assay, that quantity of copper is exactly equal to 0·150 gm. of the chemically pure copper. The quantity of nitric acid taken to dissolve 5 gm. of pure copper (266·6 c.c.) was purposely taken, so as to correspond with the quantity of 8 c.c. of special nitric acid which is applied in the assay of the copper obtained from the ore, and this quantity of acid is exactly met with in 30 c.c. of the solution of pure copper.

The influence of double quantities of ammonium nitrate and free caustic ammonia (the quantity of copper remaining the same) is shown as follows :—

(*a*) 30 c.c. of the normal solution of copper, containing exactly 0·150 gm. of copper, were rendered alkaline with 10 c.c. of special ammonia, and were found to require, for entire decoloration, 29·8 c.c. of cyanide. A second experiment, again with 30 c.c. of copper solution, and otherwise under identically the same conditions, required 29·9 c.c. of cyanide. The average is 29·85 c.c.

(*b*) When to 30 c.c. of the copper solution first 8 c.c. of special nitric acid are added, and then 20 c.c. of special ammonia instead of only 8, whereby the quantity of free ammonia and of ammonium nitrate is double what it was in the case of *a*, there is required of the same cyanide 30·0 c.c. to produce decoloration. A repetition of the experiment, under exactly the same conditions, gave 30·4 c.c. of the cyanide; the average is, therefore, 30·35 c.c. The difference amounts to only 0·05 per cent. of copper, which may be allowed for in the final calculation.

When, however, large quantities of ammoniacal salts are present in the fluid to be assayed for copper by means of cyanide, and especially when ammonium carbonate, sulphate, and, worse still, chloride are simultaneously present, these salts exert a very disturbing influence.* The presence of lead in the copper solution to be assayed has the effect of producing, on the addition of 10 c.c. of normal ammonia, a milkiness with the blue tint; but this does not at all interfere with the determination of the copper by means of the cyanide, provided the lead be not in great excess; and a slight

* I have retained this technical process in its original form, notwithstanding the use of ammonia, because it is systematic, and the results obtained by it are all comparable among themselves. Of course soda or potash may be used in place of ammonia, if the cyanide is standardized with them.

milkiness of the solution even promotes the visibility of the approaching end of the operation.

Steinbeck made some experiments purposely to test this point, and his results show that a moderate quantity of lead has no influence.

Experiments were also carefully made to ascertain the influence of zinc, the result of which showed that up to 5 per cent. of the copper present, the zinc had no disturbing action ; but a considerable variation occurred as the percentage increased above that proportion. Care must, therefore, always be taken in washing the spongy copper precipitated from the ore solution by means of zinc.

The titration must always take place at ordinary temperatures, since heating the ammoniacal solution while under titration to 40° or 45° C. considerably reduces the quantity of cyanide required.

9. Determination of Copper Colorimetrically.

This method can be adopted with very accurate results, as in the case of iron, and is available for slags, poor cupreous pyrites, waters, etc.*

The reagent used is the same as in the case of iron, viz., potassium ferrocyanide, which gives a purple-brown colour with very dilute solutions of copper. This reaction, however, is not so delicate as it is with iron, for 1 part of the latter in 13,000,000 parts of water can be detected by means of potassium ferrocyanide ; while 1 part of copper in a neutral solution, containing ammonium nitrate, can only be detected in 2,500,000 parts of water. Of the coloured reactions which copper gives with different reagents, those with sulphuretted hydrogen and potassium ferrocyanide are by far the most delicate, both showing their respective colours in 2,500,000 parts of water.

Of the two reagents sulphuretted hydrogen is the more delicate ; but potassium ferrocyanide has a decided advantage over sulphuretted hydrogen in the fact that lead, when not present in too large quantity, does not interfere with the depth of colour obtained, whereas to sulphuretted hydrogen it is, as is well known, very sensitive.†

And though iron if present would, without special precaution being taken, prevent the determination of copper by means of ferrocyanide ; yet, by the method described below, the amounts of these metals contained together in a solution can be determined by this reagent.

Ammonium nitrate renders the reaction much more delicate ; other salts, as ammonium chloride and potassium nitrate, have the same effect.

The method of analysis consists in the comparison of the purple-

* Carnelly, *C. N.* 32, 308.

† In colour titrations of this character it is essential that the comparisons be made under the same circumstances as to temperature, dilution, and admixture of foreign substances, otherwise serious errors will arise.

brown colours produced by adding to a solution of potassium ferrocyanide—first, a solution of copper of known strength; and, second, the solution in which the copper is to be determined.

The solutions and materials required are as follows :—

(1) Standard copper solution.—Prepared by dissolving 0·393 gm. of pure $CuSO_4$, $5H_2O$ in one litre of water. 1 c.c. = 0·1 mgm. Cu.

(2) Solution of ammonium nitrate.—Made by dissolving 100 gm. of the salt in one litre of water.

(3) Potassium ferrocyanide solution—1 : 25.

(4) Two glass cylinders holding rather more than 150 c.c. each, the point equivalent to that volume being marked on the glass. They must both be of the same tint, and as colourless as possible.

A burette, graduated to $\frac{1}{10}$ c.c. for the copper solution; a 5 c.c. pipette for the ammonium nitrate; and a small tube to deliver the ferrocyanide in drops.

Method of Procedure: Five drops of the potassium ferrocyanide are placed in each cylinder, and then a measured quantity of the neutral solution in which the copper is to be determined is added to one of them, and both filled up to the mark with distilled water, 5 c.c. of the ammonium nitrate solution added to each, and then the standard copper solution run gradually into the other till the colours in both cylinders are of the same depth, the liquid being well stirred after each addition. The number of c.c. used is then read off. Each c.c. corresponds to 0·1 mgm. of copper, from which the amount of copper in the solution in question can be calculated.

The solution in which the copper is to be determined must be neutral; for if it contain free acid the latter lessens the depth of colour, and changes it from a purple-brown to an earthy-brown. If it should be acid, it is rendered slightly alkaline with ammonia, and the excess of the latter got rid of by boiling. The solution must not be alkaline, as the brown coloration is soluble in ammonia and decomposed by potash or soda; if it be alkaline from ammonia, this is remedied as before by boiling it off; while free potash or soda, should they be present, are neutralized by an acid, and the latter by ammonia.

Lead, when present in not too large quantity, has little or no effect on the accuracy of the method. The precipitate obtained on adding potassium ferrocyanide to a lead salt is white; and this, except when present in comparatively large quantity with respect to the copper, does not interfere with the comparison of the colours.

When copper is to be determined in a solution containing iron, the following method is adopted :—

A few drops of nitric acid are added to the solution in order to oxidize the iron, the liquid evaporated to a small bulk, and the iron precipitated by ammonia. Even when very small quantities of iron are present, this can be done easily and completely if there be only a very small quantity of fluid. The precipitate of ferric oxide is then filtered off, washed once, dissolved in nitric acid, and re-precipitated by ammonia, filtered and washed. The iron precipitate is now free from copper, and in it the iron can be determined by dissolving in nitric acid, making the solution nearly neutral with ammonia, and determining the iron by the method on p. 238. The filtrate from the iron precipitate is boiled till the ammonia is completely driven off, and the copper determined in the solution so obtained as already described.

When the solution containing copper is too dilute to give any coloration directly with ferrocyanide, a measured quantity of it must be evaporated to a small bulk, and filtered if necessary; and if it contain iron, also treated as already described.

In the determination of copper and iron in water, for which the method is specially applicable, a measured quantity is evaporated to dryness with a few drops of nitric acid, ignited to get rid of any organic matter that might colour the liquid, dissolved in a little boiling water and a drop or two of nitric acid; if it is not all soluble it does not matter. Ammonia is next added to precipitate the iron, the latter filtered off, washed, re-dissolved in nitric acid, and again precipitated by ammonia, filtered off, and washed. The filtrate is added to the one previously obtained, the iron determined in the precipitate, and the copper in the united filtrates.

There is in use at several copper works what is known as Heines "blue test," that is an ammoniacal solution of copper, but the difficulty has been to keep strictly correct standards for comparison except they are freshly made. G. L. Heath* has solved this difficulty by making the standard from copper sulphate instead of nitrate.

METHOD OF PROCEDURE: About 0·3 gm. of pure copper is dissolved in 5 c.c. each of nitric acid (sp. gr. 1·4) and sulphuric acid (sp. gr. 1·84). Evaporate carefully till fumes of the latter acid are given off. When cold dissolve in 25 c.c. of water and add ammonia in sufficient excess to give a clear solution. This is then diluted with weak ammonia, about 1 : 6, and graduated so that each c.c. shall represent 0·0025 gm. Cu. Standards can then be made up so that 200 c.c. diluted with the weak ammonia shall contain from 0·1 to 1·3 gm. of Cu. The standards are kept in tall well-stoppered cylinders of white glass marked at 200 c.c., and when kept cool and protected from sunlight they last a long time.

The method is generally in use for lean blast furnace slags, such as contain a good deal of iron, and alumina, and lime. The method for these samples is as follows:—2·5 gm. of the finely ground material are heated in a porcelain dish with 15 c.c. of nitric acid, and after adding 5 c.c. of sulphuric acid the evaporation is continued until the mass has become a thick, but rather soft, paste; it is then treated with 70 c.c. of water to dissolve the copper sulphate, and 30 c.c. of ammonia are added. The liquid is filtered, and the residue after being twice washed with 10 c.c. of dilute ammonia (1 : 10), is rinsed back into the dish, using 50 c.c. of water, taking care not to damage the filter, and enough sulphuric acid is added to re-dissolve the iron and alumina; 25 c.c. of ammonia are again added, and the filtrate and ammoniacal washings are mixed with the main filtrate, which is then transferred to one of the tall cylinders of thin, colourless glass, and made up with dilute ammonia to 200 c.c. The colour of the liquid is compared with those of a series of copper solutions of known strength contained in similar cylinders. The colour is best seen by placing the sample and standard cylinder in front of a window, and with a piece of white paper behind them.

10. Determination by Titration of Copper Ferrocyanide with Potassium Cyanide.

Sanchez† has recently devised the following process, which is applicable in presence of tin, arsenic, antimony and organic

* *J. Am. C. S.* **19**, 21. † *Bull Soc. Chim.*, 1910, **7**, 9.

acids, but iron, lead, zinc, nickel, cobalt, manganese, and ammonium salts must be absent. The method is based on the fact that when copper ferrocyanide is dissolved in a solution of potassium cyanide a very sharp change of colour accompanies the reaction, which is as follows :—

$$Cu_2FeCy_6 + 6KCy = K_4FeCy_6 + 2(CuCy_2, KCy).$$

The solution must be exactly neutral.

METHOD OF PROCEDURE : The nitric acid solution of copper is first evaporated to dryness with sulphuric acid, any lead sulphate filtered off after adding cold water to the residue, and the copper is precipitated as Cu_2S by acidifying with H_2SO_4 and boiling with 10-20 c.c. of a 50 % solution of sodium thiosulphate. The precipitate is washed with boiling water, dissolved in nitric acid, the excess of acid boiled off, and the solution made up to a known volume. An aliquot portion of this is titrated with standard alkali, using methyl orange as indicator (or phenolphthaleïn when organic acids are present), and the amount of alkali found is added to another such portion, potassium ferrocyanide added, and the titration with potassium cyanide then proceeded with. The standard cyanide solution (6·5 gm. KCy per litre) is standardized against a solution containing 1 gm. of copper per litre. To 10 c.c. of the latter solution 1 c.c. of a 10 % solution of potassium ferrocyanide is added, and the cyanide solution is carefully run in from a burette until the reddish-brown colour suddenly changes to greenish-yellow.

CYANOGEN.

$CN = 26·01.$

1 c.c. $^N/_{10}$ silver solution	=	0·005202 gm.	Cyanogen.
,, ,,	=	0·005404 gm.	Hydrocyanic acid.
,, ,,	=	0·013022 gm.	Potassium cyanide.
,, $^N/_{10}$ iodine solution	=	0·003255 gm.	Potassium cyanide.

1. By Standard Silver Solution (Liebig).

THIS ready and accurate method of determining cyanogen in hydrocyanic acid, alkali cyanides, etc., was discovered by Liebig, and is fully described in *Ann. der Chem. und Pharm.* lxxvii. 102. It is based on the fact that when a solution of silver nitrate is added to an alkali solution containing cyanogen, with constant stirring, no permanent precipitate of silver cyanide appears until all the cyanogen has combined with the alkali and the silver to form a soluble double salt (in the presence of potash, for example, KCy, AgCy). If the slightest excess of silver, over and above the quantity required to form this combination, be added, a permanent precipitate of silver cyanide is produced, the double compound being destroyed. If, therefore, the silver solution be of known strength, the quantity of cyanogen present is easily found ; 1 eq. of silver in this case being equal to 2 eq. cyanogen.

So fast is this double combination that, when sodium chloride is present, no permanent precipitate of silver chloride is produced

until the quantity of silver necessary to form the compound is slightly overstepped.

Siebold, however, has pointed out that this process, in the case of free hydrocyanic acid, is liable to serious errors unless the following precautions are observed :—

(*a*) The solution of sodium or potassium hydrate should be placed in the beaker first, and the hydrocyanic acid added to it from a burette dipping into the alkali. If, instead of this, the acid is placed in the beaker first, and the alkali hydrate added afterwards, there may be a slight loss by evaporation, which becomes appreciable whenever there is any delay in the addition of the alkali.

(*b*) The mixture of hydrocyanic acid and alkali should be largely diluted with water before the silver nitrate is added. The most suitable proportion of water is from ten to twenty times the volume of the officinal or of Scheele's acid. With such a degree of dilution, the final point of the reaction can be observed with greater precision.

(*c*) The amount of alkali used should be as exactly as possible that required for the conversion of the hydrocyanic acid into alkali cyanide, as either an insufficiency or an excess affects the accuracy of the result. It is advisable to make first a rough estimation with excess of soda as a guide, then finish with a solution as neutral as possible. As a guide to the neutrality, or rather the slight amount of alkalinity of the solution, a little indicator C_4B* may be used, which gives a red colour with alkali hydroxides, but is not acted upon by HCy or alkali cyanides.

The volume taken for titration should not contain more than 0·1 gm. HCN. For this quantity use 5 c.c. $^{N}/_{1}$ alkali and 0·5 gm. sodium bicarbonate. Titrate over black paper. This method is useless for the determination of cyanogen in double cyanides and in mercuric cyanide.

For the determination of cyanide in presence of chloride, proceed as follows :—

Determine the cyanide by Liebig's method, add more than enough standard silver nitrate solution to combine with the chloride, acidify with nitric acid, make up to a definite volume, filter through a dry filter, and titrate the excess of silver in an aliquot portion of the filtrate by Volhard's method.

Caution.—In using the pipette for measuring hydrocyanic acid, it is advisable to insert a plug of cotton wool, slightly moistened with silver nitrate, into the upper end, so as to avoid the danger of inhaling any of the highly poisonous acid ; otherwise it is decidedly preferable to weigh it.

2. By Standard Mercuric Chloride (Hannay).

This convenient method is fully described by the author,† and is well adapted for the technical examination of commercial cyanides, etc., giving good results in the presence of cyanates, sulphocyanates, alkali salts, and compounds of ammonia and silver.

The standard solution of mercury is made by dissolving 13·537 gm.

* See p. 46. † *J. C. S.* 1878, 245.

$HgCl_2$ in water, and diluting to a litre. Each c.c. = 0·00651 gm. of potassium cyanide or 0·002611 gm. Cy.

METHOD OF PROCEDURE: The cyanide is dissolved in water, and the beaker placed upon black paper or velvet; ammonia is then added in moderate quantity, and the mercuric solution cautiously added with constant stirring until a bluish-white opalescence is permanently produced. With pure substances the reaction is very delicate, but not so accurate with impure mixtures occurring in commerce.

3. By Iodine (Fordos and Gelis).

This process, which is principally applicable to alkaline cyanides, depends on the fact that when a solution of iodine is added to one of potassium cyanide the colour of the iodine solution is discharged so long as any undecomposed cyanide remains. The reaction may be expressed by the following equation:—

$$KCN + I_2 = KI + ICN.$$

Therefore, 2 eq. iodine represent 1 eq. cyanogen in combination; so that 1 c.c. of $^N/_{10}$ iodine expresses the half of $\frac{1}{10{,}000}$ eq. cyanogen or its compounds. The end of the reaction is known by the yellow colour of the iodine solution becoming permanent. Starch indicator must not be used.

Commercial cyanides are, however, generally contaminated with caustic or monocarbonate alkalies, which would destroy the colour of the iodine like the cyanide; consequently these must be converted into bicarbonates, which is best done by adding carbonic acid water (ordinary soda water).

EXAMPLE: 5 gm. of potassium cyanide were weighed and dissolved in 500 c.c. water; then 5 c.c. (= 0·05 gm. cyanide) taken with a pipette, diluted with about $\frac{1}{4}$ litre of water, 100 c.c. of soda water added, then $^N/_{10}$ iodine delivered from the burette until the solution possessed a slight but permanent yellow colour: 12·75 c.c. were required, which multiplied by 0·003255 gave 0·0415 gm., or 83 per cent. real cyanide. Sulphides must of course be absent.

4. By $^N/_{10}$ Silver and Chromate Indicator.

Vielhaber* has shown that weak solutions of prussic acid, such as bitter-almond water, etc., may be readily titrated by adding magnesium hydrate suspended in water until alkaline, adding a drop or two of chromate indicator, and delivering in $^N/_{10}$ silver until the red colour appears, as in the case of titrating chlorides. 1 c.c. silver solution = 0·002702 gm. HCy.

This method may be found serviceable in the examination of opaque solutions of hydrocyanic acid, such as solutions of bitter-almond oil, etc.; but of course the absence of chlorine must be ensured, or, if present, the amount must be allowed for.

It is preferable to add the HCy solution to a mixture of magnesia and chromate, then immediately to titrate with silver.

* *Arch. Pharm.* [3] 13, 408.

5. Cyanides used in Gold Extraction.

An interesting series of papers on this subject have been contributed by Clennell* and Bettel.† The experiments carried out by these chemists are far too voluminous to be reproduced here, but a short summary of the results may be acceptable for the technical examination of the original solutions and their nature after partial decomposition and admixture with zinc and other impurities which naturally occur in the processes of gold extraction. The results obtained by both chemists point to the fact that the determination of cyanide in the weak solutions used in the MacArthur-Forrest process is much hampered by zinc double cyanide, by thiocyanates, also by ferro- and ferricyanides, together with organic matters which occur in the liquors after leaching the ores. According to Clennell the presence of ferrocyanides gives too high a result when the silver process of Liebig is used, but is not of much consequence unless the cyanide is relatively small as compared with the ferrocyanide ; with the iodine process the interference of ferrocyanide is much less, and very fair technical results may be obtained in the presence of both ferro- and ferri- salts by this process. The silver process appears to be fairly serviceable where the quantity of ferrocyanide is not too large ; the reddish precipitate which forms at first from the ferri- salt is soluble in the presence of excess of cyanide, and a definite end-reaction can be obtained. Thiocyanates render the silver process useless, but do not interfere with the iodine process. Ammonium carbonate interferes with the silver process unless potassium iodide is added so as to produce silver iodide, which is insoluble in the ammonia salt. Ferrocyanides, in the absence of other reducing agents, may be accurately determined, as on p. 217 ; the presence of cyanides and ferricyanides does not seriously interfere. Ferricyanides may be determined as on p. 220 ; ferrocyanides do not seriously interfere, but cyanides render the results somewhat low. These remarks apply to solutions not complicated by admixture of zinc or other matters which naturally occur in the cyanide liquors after they have been in contact with the ore. For the actual methods which have been found useful in examining the usual cyanide liquors the following processes, devised by Bettel, are given not as being absolutely correct, but sufficiently so for technical purposes, and occupying little time in the working :—

It is necessary to state at the outset that the following remarks have reference to the MacArthur-Forrest working solutions containing zinc, an element which complicates the analysis in a truly surprising manner. Before dealing with the analysis proper, attention is drawn to the peculiarities of a solution of the double cyanide of zinc and potassium, usually written K_2ZnCy_4. As is stated in works on chemistry, this cyanide is alkaline to indicators. Now here lies the peculiarity. To phenolphthalein the alkalinity, as tested by $^N/_{10}$ acid, is equal to 19·5 parts of cyanide of potassium out of a possible 130·2 parts. With methyl orange as indicator, the whole of the metallic cyanide may be decomposed by $^N/_{10}$ acid, as under :—

$$K_2ZnCy_4 + 4HCl = ZnCl_2 + 2KCl + 4HCy.$$

* *C. N.* 77, 227. † *Ibid* 286, 298.

On titration with silver nitrate solution the end-reaction is painfully indefinite. If caustic alkali in excess (a few c.c. normal soda) be added to a known quantity of potassium zinc cyanide solution together with a few drops of potassium iodide, and standard silver solution added to opalescence, the reaction will indicate sharply the total cyanogen present in the double cyanide even in the presence of ferrocyanides. If to a solution of potassium zinc cyanide be added a small quantity of ferrocyanide of potassium, and the silver solution added, the flocculent precipitate of what is supposed to be normal zinc ferrocyanide (Zn_2FeCy_6) appears, the end-reaction is fairly sharp, and indicates 19·5 parts of potassium cyanide out of the actual molecular contents of 130·2 KCy. If, however, an excess of ferrocyanide be present, the flocculent precipitate does not appear, but in its place one gets an opalescence which speedily turns to a finely granular (sometimes slimy) precipitate of potassium zinc ferrocyanide $K_2Zn_3Fe_2Cy_{12}$. This introduces a personal equation into the analysis of such a solution, for if the silver solution be added rapidly the results are higher than if added drop by drop, as this ferrocyanide of zinc and potassium separates out slowly in dilute solutions that are alkaline or neutral to litmus paper.

For the determination of free hydrocyanic acid use is made of Siebold's ingenious method for determining alkalies in carbonates and bicarbonates, by reversing the process, adding bicarbonate of soda, free from carbonate, to the solution to be titrated for hydrocyanic acid and free cyanide. This is the one instance where hydrocyanic acid replaces carbonic acid in its combinations, and as such is interesting.

$$2KHCO_3 + AgNO_3 + 2HCy = KAgCy_2 + KNO_3 + 2CO_2 + 2H_2O.$$

The methods of analysis are as follows:—

1. **Free Cyanide.**—50 c.c. of solution are taken and titrated with silver nitrate to faint opalescence or first indication of a flocculent precipitate. This will indicate (if sufficient ferrocyanide be present to form a flocculent precipitate of zinc ferrocyanide) the free cyanide, and cyanide equal to 7·9 per cent. of the potassium zinc cyanide present.

W. J. Sharwood,* after criticising the various processes in use, recommends the following scheme. To the solution containing the cyanogen, 5 c.c. of ammonia and 2 c.c. of a 5 per cent. solution of potassium iodide are added, and then standard solution of silver nitrate until a faint, permanent cloudiness is produced. If the solution contains sulphides in small amount, 5-10 c.c. of a solution made by dissolving 0·5 gm. of iodine and 2 gm. of potassium iodide in 100 c.c. of water is used in place of the potassium iodide, but a special check should be made in such case. If the amount of sulphide is large, it must be removed by means of a solution of sodium plumbite; an aliquot part of the filtrate is then titrated.

If zinc is present, a large excess of alkali should be added; in this case, the cyanogen found represents, not only the potassium cyanide, but also the double zinc compound. By determining the zinc, the amount of free potassium cyanide may be readily calculated, as ·1 part of zinc corresponds to 4 parts of potassium cyanide. A similar allowance must be made if small quantities of copper are present. If calcium, magnesium, or manganese is present, ammonium chloride must be added, whilst soda is used in presence of aluminium or lead.

For technical purposes, it is best to prepare a silver nitrate solution containing 1·305 gm. of this salt per 100 c.c.; taking samples of 10 c.c. each, ·1 c.c. of the silver represents 0·1 per cent. of potassium cyanide.

2. **Hydrocyanic Acid.**—To 50 c.c. of the solution add a solution of alkali bicarbonate, free from carbonate or excess of carbonic acid. Titrate as for free cyanide. Deduct the first from the second result, =HCy.

$$1 \text{ c.c. } AgNO_3 = \frac{0·04145}{5} = 0·00829\ \%\ HCy.$$

3. **Double Cyanides.**—Add excess of normal caustic soda to 50 c.c. of

* *J. Am. C. S.*, 1897, 400-434.

solution and a few drops of a 10 per cent. solution of KI, titrate to opalescence with $AgNO_3$. This gives 1, 2, and 3. Deduct 1 and $2 = K_2ZnCy_4$ as KCy less 7·9 per cent.

A correction is here introduced. The KCy found in 3 is calculated to K_2ZnCy_4. Factor: KCy (as K_2ZnCy_4) $\times$ 0·9423 $= K_2ZnCy_4$. Add to this 7·9 per cent. of total, or for every 92·1 parts of K_2ZnCy_4 add 7·9 parts. If this fraction, calculated back to KCy, be deducted from 1, the true free cyanide (calculated to KCy) is obtained.

4. **Ferrocyanides and Thiocyanates.**—In absence of organic matters it is found that an acidified solution of a simple cyanide, such as KCy, or a double cyanide (as K_2ZnCy_4), *i.e.*, solution of HCy, is not affected by dilute permanganate. On the other hand, acidified solutions of ferrocyanides and sulphocyanides are rapidly oxidized—the one to ferrocyanide, the other to $H_2SO_4 + HCy$.

If, now, the ferrocyanogen be removed as Prussian blue, by ferric chloride in an acid solution, the filtrate will contain ferric and hydric thiocyanate, both of which are oxidized by permanganate as if iron were not present; by deducting the smaller from the larger result, we get the permanganate consumed in oxidizing ferrocyanide, the remainder equals the permanganate consumed in oxidizing thiocyanate.

The method of titration is as follows (in presence of zinc):—A burette is filled with the cyanide solution for analysis, and run into 10 or 20 c.c. $^N/_{100}$ $K_2Mn_2O_8$ strongly acidified with H_2SO_4 until colour is just discharged. Result noted (a)

A solution of ferric sulphate or chloride is acidified with H_2SO_4 and 50 c.c. of the cyanide solution poured in. After shaking for about half a minute, the Prussian blue is separated from the liquid by filtration, and the precipitate and filter-paper washed. The filtrate is next titrated with $^N/_{100}$ $K_2Mn_2O_8$ (b).

Let (c) = c.c. permanganate required to oxidize ferrocyanide.

Then $a - b = c$.

(c) 1 c.c. $^N/_{100}$ $K_2Mn_2O_8$ = 0·003684 gm. K_4FeCy_6.
(d) 1 c.c. $^N/_{100}$ $K_2Mn_2O_8$ = 0·0001618 gm. KCNS.

5. **Oxidizable Organic Matter in Solution.**—In treating spruit tailings, or material containing decaying vegetable matter, the following method is used for testing coloured solution.

(a) Prepare a solution of a thiocyanate so that 1 c.c. = $^N/_{100}$ $K_2Mn_2O_8$.

(b) To 50 c.c. solution add sulphuric acid in excess, and then a large excess of $^N/_{100}$ permanganate. Keep at 60-70° C. for an hour. Then cool and titrate back with the KCNS solution.

Result Oxygen consumed in oxidizing organic matter.
" " " " K_4FeCy_6.
" " " " KCNS.

After determining KCNS and K_4FeCy_6, a simple calculation gives the oxygen to oxidize organic matter. This result multiplied by 9 will give approximately the amount of organic matter present.

In order to clarify such organically charged solutions, they are shaken up with powdered quicklime and filtered; the solution is then of a faint straw colour, and is in a proper condition for analysis. In such clarified solution the oxidizable organic matter is no longer present, and the determinations are readily performed.

6. **Alkalinity.**—Potassium cyanide acts as caustic alkali when neutralized by an acid; the end-reaction, however, is influenced to some extent by the hydrocyanic acid present, and is therefore not sharp. It is possible, however, to determine by $^N/_{10}$ acid:—

100 % KCy .. .. .. 7·9 % of K_2ZnCy_4	With phenolphthalein as indicator.
100 % of zinc in K_2ZnCy_4 100 % of Zn + K in ZnK_2O_2	With methyl orange as indicator.
The K_2O in ZnK_2O_2 ..	With phenolphthalein as indicator.

It will be necessary to point out the decompositions which result from adding alkali, or a carbonate of an alkali, to a working solution containing zinc.

$$K_2ZnCy_4 + 4KHO = ZnK_2O_2 + 4KCy.$$
$$K_2ZnCy_4 + 4Na_2CO_3 + 2H_2O = 2KCy + 2NaCy + ZnNa_2O_2 + 4NaHCO_3.$$

Bicarbonates have no action upon potassium or sodium zinc cyanide.

Potassium or sodium zinc oxide (in solution as hydrate) acts as an alkali towards phenolphthalein and methyl orange.

$$ZnK_2O_2 + 4HCl = 2KCl + ZnCl_2 + 2H_2O.$$

Calcium and magnesium hydrates decompose the double salt of K_2ZnCy_4 to some extent, but not completely, so that it is possible to find in one and the same solution a considerable proportion of alkalinity towards phenolphthalein, due to calcium hydrate in presence of K_2ZnCy_4.

The total alkalinity as determined by $^N/_{10}$ acid with methyl orange as indicator gives, in addition to those before mentioned, the bicarbonates. If to a solution containing sodium bicarbonate and potassium zinc cyanide be added lime, or lime and magnesia, the percentage of cyanide will increase, the zinc remaining in solution as zinc sodium oxide.

Clennell* gives a method for the approximate determination of alkali hydrates and carbonates in the presence of alkali cyanides, as follows :—

(1) Determination of the cyanide by direct titration with silver.

(2) Determination of the hydrate and half the carbonate of alkali on adding phenolphthalein to the previous solution (after titration with silver) by $^N/_{10}$ hydrochloric acid.

(3) Determination of the total alkali by direct titration, in another portion of the solution, with $^N/_{10}$ hydrochloric acid and methyl orange.

7. **Ferricyanide Determination.**—This is effected by allowing sodium amalgam to act for fifteen minutes on the solution in a narrow cylinder, then determining the ferrocyanide formed by permanganate in an acid solution. Deduct from the results obtained the ferrocyanide and thiocyanate previously found, 1 c.c. $^N/_{100}$ permanganate = 0·003293 gm. $K_6Fe_2Cy_{12}$.

8. **Sulphides.**—It rarely happens that sulphides are present in a cyanide solution ; if present, however, shake up with precipitated carbonate of lead, filter, and titrate with $^N/_{100}$ permanganate. The loss over the previous determination (of K_4FeCy_6, KCNS, etc.) is due to elimination of sulphides.

$$1 \text{ c.c. } ^N/_{100}\ K_2Mn_2O_8 = 0{\cdot}00017 \text{ gm. } H_2S, \text{ or } 0{\cdot}00055 \text{ gm. } K_2S.$$

The hydrogen alone being oxidized by dilute permanganate in acid solution where the permanganate is not first of all in excess.

9. **Ammonia.**—If sufficient silver nitrate be added to a solution (say 10 c.c.) wholly to precipitate the cyanogen compounds and a drop or two of $^N/_1$ HCl be added, the whole made up to 100 c.c., and filtered ; then 10 c.c. distilled with about 150 c.c. of ammonia-free water and Nesslerized in the usual way, the amount of ammonia may be ascertained.

10. **Copper.**—This metal appears to be in some cases a serious obstacle in the working of cyanide processes, and Clennell has devised a method of determining it which gives good technical results when not less than 0·02 gm. of the metal is present in the cyanide solution to be examined, and where zinc, iron, and silver are not present sulphocyanides and ammonium salts do not materially interfere.†

This method depends upon the facts—

(1) That cyanide of copper is precipitated from solutions of the double cyanides of copper by the addition of dilute mineral acids.

* *C. N.* **71**, 93. † *J. S. C. I.* **19**, 14.

(2) That hydrocyanic and carbonic acids have little or no action on methyl orange.

(3) That when an acid is added gradually to a mixture of a double cyanide of copper with free alkali cyanides and caustic or carbonated alkalies, no precipitation of the copper takes place until the whole of the alkalies and free cyanides have been neutralized, the first appearance of a permanent white precipitate of copper cyanide corresponding precisely with the point at which the solution becomes alkaline to methyl orange.

METHOD OF PROCEDURE: A measured volume (say from 10 to 50 c.c.) of the liquid to be tested, which must be perfectly clear and transparent, is placed in a 100 c.c. measuring flask, and $^N/_{10}$ sulphuric acid is added drop by drop from a burette with continual shaking until the turbidity formed ceases to disappear, but leaves the liquid slightly milky. The reading of the burette must now be carefully noted. This point is in general perfectly sharp and definite. A further quantity of sulphuric acid is now added, more than sufficient to precipitate the whole of the copper. (This may be ascertained if necessary by a preliminary experiment. A little of the liquid is filtered off. If the filtrate gives no further precipitation on addition of more sulphuric acid, and if it is distinctly acid to methyl orange, the reaction may be considered complete.)

The copper being thrown down as a white curdy precipitate of copper cyanide, and a slight excess of sulphuric acid being present, the reading of the burette is again taken.

The 100 c.c. flask is now filled up to the mark with distilled water and the contents thoroughly agitated. The precipitate generally settles rapidly in a flocculent condition. Now filter off 50 c.c. of the supernatant liquid, taking care to use a filter-paper free from iron or other substances soluble in acids.

The filtered liquid is now titrated with the addition of a single drop of methyl orange of 0·25 per cent. strength, using $^N/_{10}$ sodium carbonate, until the pink colour changes to a scarcely perceptible yellowish tinge.

The number of c.c. of sodium carbonate used, multiplied by 2, gives us very approximately the equivalent of the excess of sulphuric acid beyond that required to precipitate the copper.

The operations are very simple, the essential points being to note carefully the exact point at which permanent precipitation of copper cyanide takes place, the amount of acid added beyond this point, and the precise amount of sodium carbonate added. The end-point with methyl orange leaves something to be desired in point of sharpness, but by carrying out the test exactly as described and arranging matters so that the final bulk of solution is about 60 to 70 c.c., results may be obtained which are more than sufficiently accurate for any technical purpose. The actual value of the $^N/_{10}$ acid on copper may be ascertained by dissolving a known weight of pure copper in nitric acid, boiling to expel nitrous fumes, neutralizing with caustic soda, then adding cyanide until a clear and colourless solution is obtained, and titrating with the acid as above described.

Where interfering metals are present it becomes necessary to eliminate them before making the test, and this would seem at first sight a serious limitation to the usefulness of the method. Experience with a large number of ores and tailings has shown, however, that, owing to the extraordinarily rapid action of cyanide on copper compounds when a pure dilute solution of potassium cyanide has been allowed to leach through, or has been left in contact for a short time with a sample of cupriferous ore or tailings, the liquor drawn off contains practically no other impurity than the double cyanide of copper and potassium. In all such cases the method herein detailed may be successfully applied.

11. **Oxygen.**—The determination of this element in cyanide solutions is considered to be valuable, but it is very difficult to obtain an easy method. A process has been submitted to gold workers by A. F. Crosse.* The author's method for testing cyanide solutions for oxygen is an adaptation of Thresh's method, as described infra. Before the method can be used, all cyanides and absorbents of iodine must be removed. Hence, in practice, the author first treats

* *Jour. Chem. and Met. Soc. of S. Africa,* 1899, 107-112.

the solution to be examined with zinc sulphate. A bottle capable of holding $2\frac{1}{2}$ litres of the liquid to be tested is carefully filled and well stoppered, its exact capacity being known. 100 c.c. of the solution are withdrawn for a preliminary test, and are titrated with zinc sulphate solution (200 gm. per litre), using phenolphthalein as an indicator, the zinc solution being run into the cyanide until the magenta colour of the latter is just destroyed. The quantity of the standard zinc solution required for the bulk of the cyanide in the large bottle is calculated from this result, and the correct amount is added, without allowing air to enter with it, the stopper of the bottle being replaced as soon as possible. The mixture of cyanide and zinc sulphate is then thoroughly shaken and set aside for the resulting heavy flocculent precipitate of zinc cyanide to settle, which happens after some time, a small scum usually remaining on the surface. The clear liquor is then siphoned off without undue access of air by using a bent glass tube passing through one hole of a doubly perforated cork fitted into the bottle ; the second hole carries a short glass tube (arranged as in a washing-bottle), through which air is blown momentarily to start the action of the siphon. The end of the immersed limb of the siphon is covered with a small bag of lint, which filters off any floating particles of precipitate. Two or three (290 to 300 c.c.) pipettes full of the siphoned solution are drawn off and retained. A preliminary test of the iodine-absorbing power of the solution (due to unprecipitated double cyanides) is then made by adding to a quantity equal to that used in the test, 0·9 c.c. of sulphuric acid (half acid, half water), and a few drops of potassium iodide and starch. Dilute bromine water (1 bromine water : 2 water) is added until a blue colour is obtained. Another pipette full of the liquid is now taken, 0·9 c.c. of sulphuric acid and the required amount of bromine water (found from the preliminary experiment) are added, the stopper is put into the wide-mouthed bottle used in Thresh's test, and the pipette is turned over several times. 1 c.c. of the potassium iodide and sodium nitrite solution is then added, and the free iodine—freed in proportion to the oxygen in the solution—is determined by means of standard sodium thiosulphate.

By this method the amount of oxygen per litre in certain cyanide solutions was found to be as follows :—Solution from Siemens-Halske process before precipitation, 4·65 to 4·69 mgm. ; tap water, 7·7 mgm. ; the same tap-water with 0·2 per cent. KCy and a little ferrocyanide, 7·6 mgm. ; solution as pumped on to a leaching vat, 6·3 mgm. ; the same solution as run from the vat thirty hours later, 0·6 mgm. ; and the same from the end of the zinc boxes, 0·3 mgm.

It was afterwards discovered that the cyanide solutions contained a small quantity of nitrites. The process, therefore, was altered as follows :—Add potassium hydroxide, and then zinc sulphate ; determine the thiosulphate required by Thresh's method with clear solution decanted from precipitates formed in the closed bottle ; make a qualitative test for nitrites by acidifying a little of the clear solution with dilute sulphuric acid, and adding potassium iodide and starch ; and finally apply a correction for the nitrites and reagents used. To make this correction, pour into a very strong 350-c.c. flask, a quantity of solution equal to that used in the experiment (say 293 c.c.), add a few drops of potassium hydroxide, and close the flask with a rubber stopper having one perforation, through which is passed a glass tube with a glass stopcock. Boil the solution for a few minutes and close the stopcock. Cool the flask, and, when cold, pour the liquid into the pipette, and add the 1 c.c. of iodide-and-nitrite solution and 1 c.c. of sulphuric acid (1 : 1). Then let it stand for ten minutes, and, in the presence of coal-gas, run it into the bottle described in the previous paper, add starch, and titrate with thiosulphate. The quantity required gives the correction for nitrites and for the reagents, as the same amount of acid and of iodide and nitrite solution is used in each case.

W. J. Sharwood, chemist to the Montana Mining Company, has furnished me with some details as to cyanide solutions communicated by him to the *Engineering and Mining Journal*, 1898, p. 216, but the results are too voluminous to be shown here. The methods adopted were as follows :—

Free cyanide was determined by silver nitrate, using a few drops of 5 per cent. ferrocyanide solution as indicator. Total cyanogen was obtained by continuing the titration with silver after addition of caustic soda and a little ammonia and potassium iodide; this, however, does not include cyanogen in double cyanides of copper, silver, gold or mercury.

Calcium was determined by direct precipitation of 100 c.c. of the solution with ammonium oxalate, after addition of ammonium chloride and some excess of ammonia, the washed precipitate being usually dissolved in hot dilute sulphuric acid and titrated with permanganate; in some cases the precipitate was ignited and weighed as oxide.

For iron, copper and zinc 100 c.c. of the solution were twice evaporated with nitric acid, redissolved in dilute sulphuric, and iron precipitated by ammonia in excess, the precipitate being at once redissolved in hydrochloric acid and iron determined colorimetrically as thiocyanate, unless the quantity sufficed to allow of reduction by zinc and titration by permanganate. Copper was approximately determined by the colour of the ammoniacal filtrate from the iron. It was then removed by acidulating with sulphuric acid and heating with a strip of aluminium; the metal was then washed, redissolved in nitric acid, and determined by the iodide and thiosulphate method. The filtrate after removal of iron and copper was neutralized by sodium carbonate, acidulated with a fixed amount of hydrochloric acid, diluted to 200 c.c., heated, and zinc determined in it by ferrocyanide with uranium indicator.

Thiocyanate was determined by acidulating 10 or 20 c.c. with hydrochloric acid, adding ferric chloride, and comparing the colour with standard thiocyanate under the same conditions; in some cases ferrocyanides precipitated and required to be filtered off. Ferrocyanide was calculated from the iron found above. The methods for determination of ferrocyanides and thiocyanates, based upon oxidation by permanganate, were found to be totally unreliable when tested experimentally upon solutions containing known quantities in presence of the substances accompanying them in cyanide solutions. The colorimetric methods give fairly approximate results.

Sulphate was weighed as barium sulphate, precipitated by adding barium chloride to 100 c.c. of solution, after first adding some excess of hydrochloric acid, heating till odour disappeared, and filtering off any zinc and copper ferrocyanides, Prussian blue, or silver chloride that separated out.

The solid residue was obtained by evaporating 20 to 50 c.c. in a nickel or platinum dish; the former appears to be the less attacked by cyanide solutions and fused residues.

Alkalinity toward methyl orange was determined (*a*) by direct titration of 25 or 50 c.c. with decinormal acid, (*b*) by adding the standard acid in considerable excess, heating till all odour disappeared, and titrating back with standard alkali; the results were rendered somewhat uncertain by the precipitation of zinc compounds and ferrocyanides.

The same authority states that although the method given in the first part of these gold cyanide processes give fair results with tolerably pure substances, they become much less accurate when the solutions are much worked and old, owing to their containing organic matters, and various decomposition products of KCN.

FERRO- AND FERRI-CYANIDES.

Potassium Ferrocyanide.

$$K_4FeCy_6 + 3H_2O = 422{\cdot}36.$$

Metallic iron × 7·563 = Crystallized Potassium ferrocyanide.
Double iron salt × 1·080 = " " "

Oxidation to Ferricyanide by Permanganate (De Haen).

Ferrocyanide may be determined by potassium permanganate, by which it is converted into ferricyanide. The process is easy of application, and the results accurate. A standard solution of pure ferrocyanide should be used as the basis upon which to work, but may be dispensed with, if the operator chooses to calculate the strength of his permanganate from iron or its compounds. If the permanganate is decinormal, there is of course very little need for calculation (1 eq. = 422·36 must be used as the systematic number, and therefore 1 c.c. of $^N/_{10}$ permanganate is equal to 0·042236 gm. of yellow prussiate). The standard solution of pure ferrocyanide contains 20 gm. in the litre : each c.c. will therefore contain 0·02 gm.

METHOD OF PROCEDURE :* This method is found to give accurate results when carried out as follows: 20 c.c. of sulphuric acid (1 mol. of acid to 4 mols. of water) are added to 150-200 c.c. of the solution (containing about 1 grm. of ferrocyanide), and the mixture is titrated with $^N/_{20}$ permanganate, until the colour changes from yellowish-green to yellowish-red. Hydroferricyanic acid may also be determined by permanganate, after reduction with ferrous sulphate; but this acid is preferably determined by Mohr's method (see below), which is accurate when carried out in the following manner:—0·7 grm. of ferricyanide is dissolved in about 50 c.c. of water, and to the neutral solution are added 3 grms. of potassium iodide and 1·5 grms, of zinc sulphate (free from iron); the solution is then shaken and titrated with $^N/_{20}$ thiosulphate. The determination of hydroferrocyanic acid by oxidation with iodine and titration with thiosulphate in the presence of alkali bicarbonate (Rupp and Schiedt; *J. S. C. I.*, 1902, 1099), is found to be inaccurate.

Commercial Ferrocyanides.

Potassium	ferrocyanide,	$K_4Fe\ (CN)_6,\ 3H_2O = 422{\cdot}36$.
Sodium	,,	$Na_4Fe\ (CN)_6,\ 10H_2O = 484{\cdot}07$.
Calcium	,,	$Ca_2Fe\ (CN)_6,\ 12H_2O = 508{\cdot}28$.

All of the above are obtained as by-products in the coal-gas industry from the hydrocyanic acid present in the crude gas. The crude products in each case may consist of the soluble potassium, sodium, or calcium salt, but usually there are also present insoluble ferrocyanides in the form of double ferrocyanides of iron with these metals or ammonium, the amount of which has to be included in the analytical results. The products obtained from crude coal-gas frequently contain, in addition, appreciable quantities of the very soluble carbonyl ferrocyanide, $Na_3FeCO(CN)_5$, or sodium ferrocyanide ($Fe(CN)_2$, 4NaCN) in which one molecule of NaCN has been replaced by the radicle CO. In other cases, such as the spent oxide from gas-works, the whole of the ferrocyanide present is in an insoluble form and, before analysis, must be converted into soluble salts. This is done as follows :—

The sample is ground, thoroughly mixed, and a weighed portion (30-40 grams) put into a mortar, caustic soda in excess and about

* E. Müller and O. Diefenthaler, Z. anorg. Chem. 1910, **67**, 418-436; also, Mecklenburg, *Z. a. C.*, 1910, 322, and *J. S. C. I.*, **29**, 946.

100 c.c. of water added, and allowed to stand for several hours, with frequent trituration with the pestle. A few crystals of ferrous sulphate may also be added, to bring about the conversion of any cyanide present into ferrocyanide and the reduction of any ferricyanide to ferrocyanide. Heat should not be employed, as the products mostly contain both ammonia and sulphides or free sulphur, the latter yielding sodium sulphide by the action of the NaOH, and in hot solution the alkali sulphides, in presence of ammonia, effect a partial conversion of the ferrocyanide into sulphocyanide, thus tending to make the ferrocyanide results low. In absence of ammonia, however, boiling sodium sulphide has but little action on ferrocyanide. The mixture, when decomposition is complete, is either filtered and made up to 1 litre or it may be at once placed in a litre flask, made up to the mark, and a further addition of water made equal to the volume of the insoluble matter present: the whole is then well shaken, allowed to settle, and the clear solution taken for analysis.

Owing to the frequent presence of sulphocyanides and other oxygen-consuming bodies in the above products the old method of titration by standard permanganate is inadmissible and the two following methods are now recommended :—

1. Determination of the amount of hydrocyanic acid present (Feld).

2. Direct determination of the ferrocyanide present by titration with standard zinc or copper sulphate solution (Knublauch).

The first method is described by Dr. H. G. Colman* as the one giving the most accurate results, and is carried out as follows :—

A quantity of the solution, prepared as described above, and containing the equivalent of 0·3 – 0·5 gm. of K_4FeCy_6, is diluted with water in a large flask, mixed with 10 c.c. $^N/_1$ caustic soda, and heated to boiling: to this 15 c.c. of hot magnesium chloride solution (610 gm., $MgCl_2$, $6H_2O$ per litre) are added slowly with continual shaking in order to get a milky precipitate of magnesium hydrate, and the boiling continued for 5 minutes and no more—the object being to convert any free alkali into magnesium hydroxide. (If free cyanide is also present, the HCN in this form is then evolved, and may be condensed and collected for analysis, the boiling in that case being continued for a longer period.) 100 c.c. of boiling mercuric chloride solution (27·1 gm. $HgCl_2$ per litre) are then added, and the boiling continued for a further ten minutes, all ferrocyanide being thus converted into mercuric cyanide. The flask is then connected to a condenser, 30 c.c. of 4N sulphuric acid added by means of a stoppered funnel, and distillation continued for 20-30 minutes, the end of the condenser dipping under the surface of 25 c.c. of $^N/_1$ NaOH placed in the receiver. The solution of sodium cyanide thus obtained is now diluted to about 400 c.c., a crystal of KI added, and $^N/_{10}$ silver nitrate run in from a burette until a permanent yellow precipitate of AgI is obtained.

* *The Analyst*, 1908, **33**, 261: 1910, **35**, 295.

$$1 \text{ c.c. } {}^{N}/_{10} \text{ AgNO}_3 = 0{\cdot}005404 \text{ gram HCN}$$

and from this the amount of ferrocyanide is readily calculated.

Knublauch's method consists in titrating the ferrocyanide solution, acidified with sulphuric acid, with a standard solution of copper or zinc sulphate, using a ferric salt as indicator. If the solution contains sulphide, this is first removed by shaking with lead carbonate and filtering off the lead sulphide and the excess of lead carbonate. In order to obtain accurate results, it has been stated to be necessary to standardize the zinc or copper solution with the same salt of ferrocyanic acid as is used for the titration, owing to the influence of the soluble sulphate formed during the process. Dr. Colman* has shown, however, that, if the ferrocyanide present is not potassium ferrocyanide, by adding 50 c.c. of a cold saturated solution of potassium sulphate before titration (and the same quantity to the pure potassium ferrocyanide solution when standardizing the copper or zinc solution) excellent results are obtained. He uses standard solutions containing 10 grams crystallized copper sulphate or (its exact equivalent) 11·51 gm. of crystallized zinc sulphate per litre. A standard solution of 4 grams crystallized potassium ferrocyanide per litre, equal to 2·044 gm. ferrocyanic acid $H_4Fe\ (CN)_6$, may be used, 50 c.c. being taken for standardizing. The end-point of the titration is determined either by filtering small portions of the liquid through Swedish filter-paper and adding ferric solution to the filtrate, or placing a drop of the liquid on a Schleicher and Schüll drop reaction filter paper, followed by a drop of ferric chloride so placed as to come in contact with the clear wetted portion only of the first spot. The titration should be carried out in a good light. The amount of dilution and degree of acidity, within reasonable limits, affect the result but little.

Dr. Skirrow† recommends stronger solutions than those given above. He uses solutions of 50 gm. crystallized sodium ferrocyanide and 46·5 gm. of zinc sulphate per litre, and in making a test always acidifies with 2 c.c. of dilute H_2SO_4 (1 : 2). He states that with the more concentrated solutions a sharper end-point is obtained and that the effect of the presence of excess of alkali sulphate is minimized.

The presence of carbonyl ferrocyanide interferes with the analysis in both of the methods described above, as it is precipitated along with the ferrocyanide by both zinc and copper solutions, and the hydrocyanic acid from it is determined along with the rest by the Feld method. Dr. Colman uses a simple method of separation based on the fact that the carbonyl ferrocyanides are readily soluble in dilute alcohol whilst ferrocyanides are insoluble. To the solution of ferrocyanides, which must be alkaline or neutral, 4 or 5 times its volume of methylated spirit (industrial alcohol) is added, the mixture is allowed to stand for several hours, and

* *Loc. cit.* † *J. S. C. I.* 1910, **29**, 319.

filtered. The precipitate is washed with a little methylated spirit and dried in the water-oven. The filter paper and precipitate are then transferred to the titrating basin, water added, the liquid acidified, and then proceeded with as described above, or simply dissolved in water and treated by the Feld process.

Potassium Ferricyanide.

$K_6Fe_2Cy_{12} = 658{\cdot}42.$

Metallic iron	×	5·895	=	Potassium ferricyanide.
Double iron salt	×	1·684	=	,, ,,
$^{N}/_{10}$ Thiosulphate	×	0·03292	=	,, ,,

By Iodine and Thiosulphate.

This salt can be determined either by reduction to ferrocyanide and titration with permanganate or dichromate, or by Lenssen's method, which is based upon the fact that when potassium iodide and ferricyanide are mixed with tolerably concentrated hydrochloric acid iodine is set free.

$$K_6Fe_2Cy_{12} + 2KI = 2K_4FeCy_6 + I_2$$

the quantity of which can be determined by $^{N}/_{10}$ thiosulphate and starch. This method does not, however, give the most satisfactory results, owing to the variation produced by working with dilute or concentrated solutions. The modification given under Zinc, is, however, more accurate, and is as follows :—The ferricyanide is dissolved in a convenient quantity of water, potassium iodide in crystals added, together with hydrochloric acid in tolerable quantity, then a solution of pure zinc sulphate in excess; after standing a few minutes to allow of complete decomposition, the excess of acid is slightly over-neutralized by addition of sodium carbonate.

At this stage all the zinc ferricyanide first formed is converted into the ferrocyanide of that metal, and an equivalent quantity of iodine set free, which can at once be titrated with $^{N}/_{10}$ thiosulphate and starch, and with very great exactness. 1 c.c. $^{N}/_{10}$ thiosulphate $= 0{\cdot}03292$ gm. potassium ferricyanide.

Another method consists in boiling with excess of potash, then cooling, and adding H_2O_2 till the colour becomes yellow. The excess of the peroxide is then boiled off, H_2SO_4 added, and the solution titrated with permanganate.

Reduction of Ferri- to Ferro-cyanide.

This process is, of course, necessary when the determination by permanganate has to be made, and is best effected by boiling the weighed ferricyanide with an excess of potash or soda, and adding small quantities of concentrated solution of ferrous sulphate until the precipitate which is formed possesses a blackish colour (signifying that the magnetic oxide is formed). The solution is then diluted

to a convenient quantity, say 300 c.c., well mixed, and filtered through a dry filter; 50 or 100 c.c. may then be taken, sulphuric acid added, and titrated with permanganate as before described.

Kassner* suggests the use of sodium peroxide for the reduction of ferri- to ferro-cyanide as being rapid and complete. About 0·5 gm. in 100 c.c. water requires about 0·06 gm. of the peroxide; the mixture is heated till all effervescence is over, acidified with sulphuric acid, cooled, and titrated with permanganate in the usual way.

THIOCYANATES.

Volhard's method is described on p. 145.

For the determination of thiocyanic acid in combination with the alkali or earthy bases, Barnes and Liddle† have devised a method which is easy of application, and gives good technical results. It is not, however, available for gas liquors.

The method depends upon the fact that when a solution of a cupric salt is added to a solution of a thiocyanate in presence of a reducing agent, as sodium bisulphite, the insoluble cuprous salt of thiocyanic acid is precipitated, the end of the reaction being ascertained by a drop of the solution in the flask giving a brown colouration when brought in contact with a drop of ferrocyanide. The following reactions take place :—

$$2CuSO_4 + 2KSCN + Na_2SO_3 + H_2O = 2CuSCN + K_2SO_4 + 2NaHSO_4$$

and

$$2CuSO_4 + Ba(SCN)_2 + Na_2SO_3 + H_2O = 2CuSCN + BaSO_4 + 2NaHSO_4$$

The following solutions are required :—

1. A standard solution of copper sulphate containing 6·2375 gm. per litre, 1 c.c. of which is equivalent to 0·00145 gm. SCN.
2. A solution of sodium bisulphite of specific gravity 1·3.
3. A solution of potassium ferrocyanide (1 : 20).

METHOD OF PROCEDURE: About 3 gm. of the sample are weighed from a stoppered tube into a litre flask, dissolved in water, and made up to the mark. After well mixing, 25 c.c. are measured into a flask, about 3 c.c. of the bisulphite added, and the whole boiled. Whilst this is heating a burette is filled with the copper solution, and a white porcelain slab is spotted over with the ferrocyanide. When the liquid in the flask has reached the boiling point, 20 c.c. of the copper solution are run in, well shaken, the precipitate allowed to settle for about a minute, a drop is taken out by means of a glass rod, and brought in contact with a drop of ferrocyanide, and should no brown colouration appear, more of the copper solution is run in, say 1 c.c. at a time, and again tested. This is continued until a drop gives a colour immediately. By this means an approximation to the truth is obtained. It will be observed during a titration that the mixed drops, after standing for a minute, or even less, produce a brown tint. It is of the utmost importance that the colouration be *immediate*.

A second 25 c.c. of the thiocyanate solution are run into a clean flask, the bisulphite added, and boiled as before.

Suppose that in the first experiment, after an addition of 27 c.c. of copper

* *Arch. Pharm.* 232, 226.   † *J. S. C. I.* 2, 122.

solution, no colour was formed with ferrocyanide, but that 28 c.c. gave an immediate colour; then in the second experiment 27 c.c. are run in at once, and the liquid is again tested, when no colour should appear. The copper solution is then run in drop by drop until there is a slight excess of copper, as proved by the delicate reaction with the ferrocyanide. The second experiment is thus rendered more exact by the experience gained in the first.

According to Schroder,* thiocyanates can be determined by means of permanganate, the reaction being approximately quantitative according to the equation:

$$HSCN + O_2 = SO_2 + HCN.$$

When $^N/_{10}$ solutions are employed and when the manganese is precipitated by sodium carbonate, redissolved in HCl and again titrated. A correct determination of thiocyanic acid may, however, be made by adding a definite volume of the thiocyanate solution to a known excess of warmed permanganate solution acidified with sulphuric and phosphoric acids, decomposing the excess of permanganate by the addition of an excess of either standardized oxalic acid solution or hydrogen peroxide, and titrating the latter with permanganate.

For the determination of thiocyanates and ferrocyanides, etc., in cyanide solutions containing copper, see Green.†

GOLD.

$Au = 197{\cdot}2.$

1 c.c. of normal oxalic acid = 0·0657 gm. Gold.

The technical assay of gold for coining purposes is invariably performed by cupellation. Trichloride of gold is, however, largely used in photography and electro-gilding, and therefore it may be necessary sometimes to ascertain the strength of a solution of the chloride, or its value as it occurs in commerce.

If to a solution of gold in the form of chloride (free from nitric acid and the free hydrochloric acid nearly neutralized by ammonia) an excess of oxalic acid be added, in the course of from eighteen to twenty-four hours all the gold will be precipitated in the metallic form, while the corresponding quantity of oxalic acid has been dissipated in the form of carbonic acid; if, therefore, the quantity of oxalic acid originally added be known, and the excess, after complete precipitation of the gold, be found by permanganate, the amount of gold can be ascertained.

A more rapid method consists in boiling the neutral gold solution with an excess of standard solution of potassium oxalate containing 8·3 gm. of the pure salt per litre, and titrating back with a permanganate solution which has the same working strength as the oxalate. Each c.c. of oxalate solution decomposed represents 0·00657 gm. Au.

* *J. S. C. I.* 1909, **28**, 1066. † *J. S. C. I.* 1908, **27**, 1085.

The determination of small proportions of gold in solution can be done by iodine and thiosulphate as shown by Petersen*, and the method has been verified by F. A. Gooch and F. H. Morley.† These chemists found that the reduction of the auric salt with the consequent liberation of iodine was somewhat influenced by the volume of the solution, the amount of iodine present, and the time of action. Their experiments showed that the best effects were obtained in a solution of pure gold chloride of about 0·8 gm. of the salt to the litre by using 0·1 gm. KI to volumes of the chloride ranging between 25 and 50 c.c. The iodine and thiosulphate solutions used were about $^{N}/_{100}$ strength and verified against each other. The solution of KI contained 10 gm. per litre.

Method of Procedure: The gold solution is measured from a burette and the potassium iodide added in the proportion above mentioned; there must always be enough of this to more than redissolve the aurous iodide precipitated at first. A clear solution of starch is then added, and the blue colour produced by it is just removed by thiosulphate. The standard iodine is then added until the liquid assumes a faint rose colour, and the amount of gold is obtained. Of course the gold value of the standard solutions must be ascertained by experiment upon a pure gold solution of known strength. For very small quantities of gold $^{N}/_{1000}$ solutions of iodine and thiosulphate may be used with good effect, but in this case a correction of 0·1 c.c. for the iodine must be allowed for volumes not exceeding 30 c.c. of the gold, because that is the amount required to bring out the rose colour in a blank experiment. In the practical use of this process for the determination of metallic gold, the metal can of course be got into solution by chlorine water or aqua regia, but in the removal of the excess of the oxidizer by evaporation it is difficult to prevent the formation of aurous chloride. Gooch and Morley, however, found that by adding ammonia in excess to the solution, boiling gently, acidifying with HCl, and heating if necessary to redissolve the precipitate by ammonia, again treating with ammonia and heating, and once more acidifying, the ammonium chloride so formed acts apparently in producing a clear solution ready for titration.

Colorimetric Determination of Gold in Ores.—This method is mentioned in *Rose's Gold Metallurgy* as being of service.

Method of Procedure: Take 100 gm. of the ore, or less if more than a trace of gold, and heat it in a stoppered bottle for some hours with 10 c.c. of bromine and 100 c.c. of water. Then filter off the liquid, and wash the residue several times with water. Evaporate the filtrate till it no longer smells of bromine. Make it up to 100. c.c. and raise it to boiling. Place 5-10 c.c. of a fresh saturated solution of stannous chloride in a beaker and rapidly pour upon it the boiling extract. A precipitate will form and sink to the bottom. If no gold be present the precipitate has a slight bluish tint. Gold causes it to be purplish red to blackish purple, according to the quantity present. The gold is determined by taking small quantities of standard gold solution, making up to 100 c.c., boiling and pouring into stannous chloride, exactly as was done with the ore extract. In this way the gold can be approximately determined. The gold present should be between 0·0001 and 0·00002 gm. If there be more than 0·0001 gm. a more dilute extract of ore should be prepared. If less than 0·00002 gm. be present a larger quantity of ore should be used.

Determination of Gold in dilute Cyanide Solutions.—J. Moir‡ gives the following

* *Zeit. f. Anorg. Chem.* **19**, 63. † *Amer. Jour. Sci.*, October, 1899.
‡ *J. S. C. I.* abstr. **22**, 1257.

rapid method :—100 c.c. of the solution are boiled for two minutes with about 1 gm. of sodium peroxide, to destroy cyanides. Next, two drops of 10 per cent. lead acetate solution are added, and about 0·2 gm. of aluminium powder is stirred in. Metallic lead is thus precipitated, and the gold is also extracted by the galvanic action. The whole is filtered when the aluminium has dissolved (the filtrate being free from cyanide as well as gold). The black precipitate is dissolved in 10 c.c. of boiling 60 per cent. aqua regia, and treated carefully with stannous chloride solution until the yellow colour is bleached, whereupon the purple tint (purple of Cassius) develops, and is constant after a minute. It is then compared with a set of artificial standards, after making the liquid up to 15 c.c. in a tube of fixed diameter. The standard tubes are filled with a permanent imitation of " purple of Cassius," made by mixing copper and cobalt salts in the required proportion. They are standardized empirically. The shade is easily visible with solutions carrying 1 part of gold per million, and by looking down the tubes (as in Nesslerizing), 2 grains per ton (1 in seven millions) can be detected. Of course, even less than this can be recognised, if more than 100 c.c. of solution be used at the beginning.

IODINE.

$I = 126 \cdot 92.$

1. By Distillation.

Free iodine is of course very readily determined by solution in potassium iodide, and titration with starch and $^N/_{10}$ thiosulphate, as described on p. 128 et seq.

Combined iodine in haloid salts, such as the alkali iodides, must be subjected to distillation with hydrochloric acid and some other substance capable of assisting in the liberation of iodine, which is received into a solution of potassium iodide, and then titrated with $^N/_{10}$ thiosulphate in the ordinary way. Such a substance presents itself best in the form of ferric oxide, or some of its combinations. If, therefore, hydriodic acid, or, what amounts to the same thing, an alkali iodide, be mixed with an excess of ferric oxide or chloride and distilled in the apparatus shown in fig. 38 or 39, the following reaction occurs :—

$$Fe_2O_3 + 2HI = 2FeO + H_2O + I_2.$$

The best form in which to use the ferric oxide is iron alum.

The iodide and iron alum having been brought into the little flask (fig. 39), sulphuric acid of about 1·3 sp. gr. is added, and the cork carrying the distillation tube inserted. This tube is not carried into the solution of potassium iodide in this special case, but within a short distance of it ; and the end must not be drawn out to a fine point, as there represented, but cut off straight. The reason for this arrangement is that it is not a chlorine distillation for the purpose of setting iodine free from the iodide solution, as is usually the case, but an actual distillation of iodine, which would speedily choke up the narrow point of the tube and so prevent the further progress of the operation.

As the distillation goes on, the steam washes the condensed iodine out of the tube into the solution of iodide, which must be

present in sufficient quantity to absorb it all. When no more violet vapours are to be seen in the flask, the operation is ended; but to make sure it is well to empty the solution of iodine out of the condensing tube into a beaker, and put in a little fresh iodide solution with starch, then heat the flask again; the slightest traces of iodine may then be detected by the production of the blue colour when cooled. When this takes place the distillation is continued a little while, then both liquids are mixed, and titrated with $^{N}/_{10}$ thiosulphate as usual.

It has been previously stated that the rubber joints to the special apparatus of Fresenius, Bunsen, or Mohr for iodine distillations are objectionable. Topf* avoids this by fitting his apparatus together so that, although rubber is used the reagents do not come in contact with it.

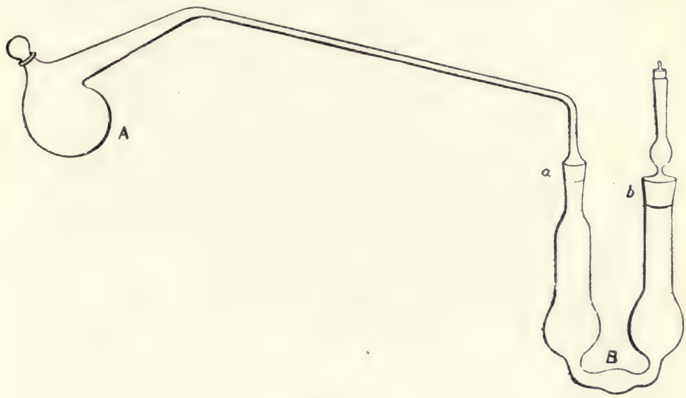


Fig. 43.

Another form of apparatus designed by Stortenbeker† is shown in fig. 43, in which rubber joints are entirely dispensed with, and glass connections alone used. The connection between the distilling tube and the absorbing apparatus is a water joint, the tube resting in a socket kept wet with water, the chloride of calcium tube is filled with glass beads, moistened with concentrated solution of potassium iodide, and the connection with the absorbing apparatus is ground in like an ordinary stopper. The absorbing bulbs are immersed in water to the middle of the bulbs, and the immersed portion partially filled with iodide solution.

Ferric chloride may be used instead of the iron alum, but it must be free from nitric acid or active chlorine (best prepared from dry Fe_2O_3 and HCl).

The iodides of silver, mercury, and copper cannot be accurately analysed in this way, but must be specially treated. They should be dissolved in the least possible quantity of sodium thiosulphate

* *Z. a. C.* **26**, 293. † *Z. a. C.* **29**, 273.

solution, and precipitated boiling with sodium sulphide, then filtered; the filtrate contains the whole of the iodine free from metal. The filtrate is evaporated to dryness and ignited, then dissolved in water, and distilled with a good excess of ferric salt.*

2. Mixtures of Iodides, Bromides, and Chlorides.

Donath† has shown that iodine may be accurately determined by distillation in the presence of other halogen salts by means of a solution containing about 2 to 3 per cent. of chromic acid free from sulphuric acid.

In the case of a mixture of iodides and chlorides the action is perfectly regular, and the whole of the iodine may be received into potassium iodide without any interference from the chlorine.

In the case of bromides being present, the chromic solution must be rather more dilute, and the distillation must not be continued for more than two or three minutes after ebullition has commenced, otherwise a small amount of bromide is decomposed.

The reaction in the case of potassium iodide may be expressed thus:

$$6KI + 8CrO_3 = 3I_2 + Cr_2O_3 + 3K_2Cr_2O_7$$

The distillation may be made in Mohr's apparatus (fig. 39), using about 50 c.c. of chromic solution for about 0·3 gm. I.

The titration is made with thiosulphate in the usual way.

A much less troublesome method of determining iodine in the presence of bromides or chlorides has been worked out by Cook,‡ and depends on the fact that hydrogen peroxide liberates iodine completely from an alkali base in the presence of excess of acetic acid, while neither bromine nor chlorine is affected.

Hydrogen peroxide alone will only partially liberate iodine from potassium iodide, but with excess of a weak organic acid to combine with the alkali hydroxide, the liberation is complete. Strong mineral acids must not be used, as bromine and chlorine, if present, would then be set free also.

METHOD OF PROCEDURE: The solution is strongly acidified with acetic acid, and sufficient hydrogen peroxide added to liberate the iodine (5 c.c. will suffice for 1 gm. KI). The mixture is allowed to stand from half an hour to an hour; the whole of the iodine separates, some being in the solid state if the quantity is considerable. Chloroform is now added in sufficient volume to dissolve the iodine, the solution siphoned off, and the globule repeatedly washed with small quantities of water to remove excess of peroxide, then titrated with thiosulphate. with or without starch, in the usual way. If the peroxide is not completely removed by washing, it will decompose the sodium iodide produced in the titration, and so liberate traces of iodine.

The results obtained by Cook in mixtures of bromides, iodides, and chlorides showed about 99 per cent. of the iodine present.

Gooch and Browning‖ publish a method of determining

* Mensel, *Z. a. C.* **12**, 137. † *Z. a. C.* **19**, 19. ‡ *J. C. S.*, 1885, 471.

‖ *Amer. Jour. Science* **39**, March, 1890, also *C. N.* **61**, 279.

iodine in halogen salts of the alkalies which gives excellent results, and which is based on the fact that arsenic acid in strongly acid solution liberates iodine, becoming itself reduced to arsenious acid, according to the equation.

$$H_3AsO_4 + 2HI = H_3AsO_3 + H_2O + I_2.$$

A series of very careful experiments are detailed in the original paper, the outcome of the whole being summarized in the following process :—

METHOD OF PROCEDURE : The substance (which should not contain of chloride more than an amount corresponding to 0·5 gm. of sodium chloride, nor of bromide more than corresponds to 0·5 gm. of potassium bromide, nor of iodide much more than the equivalent of 0·5 gm. of potassium iodide) is dissolved in water in a conical beaker of 300 c.c. capacity, and to the solution are added 2 gm. of potassium binarsenate dissolved in water, 20 c.c. of a mixture of sulphuric acid and water in equal volumes, and enough water to increase the total volume to 100 c.c. or a little more. A platinum spiral is introduced, a trap made of a straight two-bulb drying tube, cut off short, is hung with the larger end downward in the neck of the flask, and the liquid is boiled until the level reaches a mark put upon the flask to indicate a volume of 35 c.c. Great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and setting up reduction of the arsenate by the bromide. On the other hand, though 35 c.c. is the ideal volume to be attained, failure to concentrate below 40 c.c. introduces no appreciable error. The liquid remaining is cooled and nearly neutralized by sodium hydrate (ammonia is not equally good), neutralization is completed by potassium bicarbonate, an excess of 20 c.c. of the saturated solution of the latter is added, and the arsenious oxide in solution is titrated by standard iodine in the presence of starch.

With ordinary care the method is rapid, reliable, and easily executed, and the error is small. In analyses requiring extreme accuracy, all but accidental errors may be eliminated from the results by applying the following corrections. These corrections are based on a long series of experiments, which cannot well be given here, but the results may be stated shortly as follows :—

When no chloride or bromide is present the iodine may be estimated with a mean error of 0·2 mgm. in 0·5 gm. or so of the alkali iodide. When sodium chloride is present, there is a slight deficiency in iodine which is proportional to the amount of iodide decomposed. For about 0·56 gm. of potassium iodide and 0·5 gm. of sodium chloride the deficiency in iodine amounted to 0·0011 gm. When the iodide is decreased, say to one-tenth or less, the deficiency falls to 0·0002 gm. The presence of potassium bromide liberates traces of bromine, and consequently increases the AsO_3, and gives apparent excess of iodine, the mean error being 0·0008 gm. for 0·5 gm. of bromide.

The simultaneous action of the chloride and bromide tends of course to neutralize the error due to each. Thus, in a mixture weighing about 1·5 gm. and consisting of sodium chloride, potassium bromide, and potassium iodide in equal parts, the mean error amounts to $-0·0003$ gm. The largest error in the series is $+0·0016$ gm., when the bromide was at its maximum, and no chloride was

present; and the next largest was −0·0013 gm., when the chloride was at its maximum and no bromide was present.

From a series of experiments detailed in the original paper it was deduced that the amount of iodine to be added, in each case, may be obtained by multiplying the product of the weights in grams of sodium chloride and potassium iodide by the constant 0·004; and the amount to be subtracted, by multiplying the weight in grams of potassium bromide by 0·0016; but in order to make use of these corrections the approximate amounts of these salts present must be known.

3. Titration with $^N/_{10}$ Silver and Thiocyanate.

The thiocyanate and silver solutions are described on p. 145, et seq.

The iodide is dissolved in 300 or 400 times its weight of water in a well-stoppered flask, and $^N/_{10}$ silver delivered in from the burette with constant shaking until the precipitate coagulates, showing that silver is in excess. Ferric indicator and nitric acid are then added in proper proportion, and the excess of silver determined by thiocyanate as described on p. 145.

4. Oxidation of combined Iodine by Chlorine (Golfier Besseyre and Dupré).

This wonderfully sharp method of determining iodine depends upon its conversion into iodic acid by free chlorine. When a solution of potassium iodide is treated with successive quantities of chlorine water, iodine is liberated at first, then chloride of iodine (ICl) formed. If starch, chloroform, benzole, or bisulphide of carbon be added, the first will be turned blue, while any of the others will be coloured intense violet. A further addition of chlorine, in sufficient quantity, produces pentachloride of iodine (ICl_5), or rather, as water is present, iodic acid (IO_3H). No colouration of the above substances is produced by these compounds, and the accuracy with which the reaction takes place has been made use of by Golfier Besseyre and Dupré, independently of each other, for the purpose of determining iodine. The former suggested the use of starch; the latter chloroform or benzole, with very dilute chlorine water. Dupré's method is preferable on many accounts.

EXAMPLE: 30 c.c. of weak chlorine water were put into a beaker with potassium iodide and starch, and then titrated with $^N/_{100}$ thiosulphate, of which 17 c.c. were required.

10 c.c. of solution of potassium iodide containing 0·010 gm. of iodine were put into a stoppered bottle, chloroform added, and the same chlorine water as above delivered in from the burette, with constant shaking, until the red colour of the chloroform had disappeared: the quantity used was 85·8 c.c. The excess of chlorine was then ascertained by adding sodium bicarbonate, potassium iodide and starch. A slight blue colour was produced; this was removed by $^N/_{100}$ thiosulphate, of which 1·2 c.c. was used. Now, as 30 c.c. of the chlorine solution required 17 c.c., the 85·8 c.c. required 48·6 c.c. of thiosulphate. From this,

however, must be deducted the 1·2 c.c. in excess, leaving 47·4 c.c.$^{N}/_{100}$ = 4·74 c.c. of $^{N}/_{10}$ solution, which multiplied by 0·00211, the one-sixth of $\frac{1}{10000}$ eq. (1 eq. of iodic acid liberating 6 eq. iodine), gave 0·0100 gm. iodine.

Mohr suggests a modification of this method which dispenses with the use of chloroform or other similar agent.

The weighed iodine compound is brought into a stoppered flask, and chlorine water delivered from a large burette until all yellow colour has disappeared. A drop of the mixture brought in contact with a drop of starch must produce no blue colour; sodium bicarbonate is then added till the mixture is neutral or slightly alkaline, together with potassium iodide and starch; the blue colour is then removed by $^{N}/_{10}$ thiosulphate. The strength of the chlorine water being known, the calculation presents no difficulty.

Mohr obtained by this means 1·0101 gm. iodine, instead of 1·01 gm.

5. Oxidation by Permanganate (Reinige).

This process for determining iodine in presence of bromides and chlorides gives satisfactory results.

When potassium iodide and permanganate are mixed, the rose colour of the latter disappears, a brown precipitate of manganic peroxide results, and potassium hydroxide with potassium iodide remains in solution. 1 eq. I(=126·92) reacts with 1 eq. $K_2Mn_2O_8$ (=316·06), thus—

$$KI + K_2Mn_2O_8 + H_2O = KIO_3 + 2KOH + 2MnO_2.$$

Heat accelerates the reaction, and it is advisable, especially with weak solutions, to add a small quantity of potassium carbonate to increase the alkalinity. No organic matter must be present.

The permanganate and thiosulphate solutions required in the process may conveniently be of $^{N}/_{10}$ strength, but their reaction upon each other must be definitely fixed by experiment as follows:—2 c.c. of permanganate solution are freely diluted with water, a few drops of sodium carbonate added, and the thiosulphate added in very small portions until the rose colour is just discharged. The slight turbidity produced by the precipitation of hydrated manganic oxide need not interfere with the observation of the exact point.

Method of Procedure: The iodine compound being dissolved in water, and always existing only in combination with alkali or alkaline earthy bases, is heated to gentle boiling, rendered alkaline with sodium or potassium carbonate, and permanganate added till in distinct excess, best known by removing the liquid from the source of heat for a minute, when the precipitate will subside, leaving the upper liquid rose-coloured; the whole may then be poured into a 500-c.c. flask, cooled, diluted to the mark, and 100 c.c. taken out for titration with thiosulphate. The amount so used, being multiplied by 5, will give the proportion required for the whole liquid, whence can be calculated the amount of iodine. To prove the accuracy of the process in a mixture of iodides, bromides, and chlorides, with excess of alkali, the following experiment was made. 7 gm. commercial potassium bromide, the same quantity of sodium chloride, with 1 gm. each of potassium hydrate and carbonate, were dissolved in a convenient quantity of water, and heated to boiling; permanganate was then added cautiously to destroy the traces of iodine

and other impurities affecting the permanganate so long as decolouration took place; the slightest excess showed a green colour (manganate). To the mixture was then added 0·1246 gm. pure iodine, and the titration continued as described: the amount found was 0·125 gm. I.

With systematic solutions of permanganate and thiosulphate the calculation is as follows:—

$$1 \text{ c.c. } {}^{N}/_{10} \text{ solution} = 0{\cdot}012692 \text{ gm. I.}$$

6. By Nitrous Acid and Carbon Disulphide (Fresenius).

This process requires the following standard solutions:—

(*a*) Potassium iodide, about 5 gm. per litre.

(*b*) Sodium thiosulphate, $\frac{1}{20}$ normal, 12·4 gm. per litre, or thereabouts.

(*c*) Nitrous acid, prepared by passing the gas into tolerably strong sulphuric acid until saturated.

(*d*) Pure carbon disulphide.

(*e*) Solution of sodium bicarbonate, made by dissolving 5 gm. of the salt in 1 litre of water, and adding 1 c.c. of hydrochloric acid.

METHOD OF PROCEDURE: The strength of the sodium thiosulphate in relation to iodine is first ascertained by measuring 50 c.c. of the iodide solution into a 500 c.c. stoppered flask, then about 150 c.c. water, 20 c.c. carbon disulphide, then dilute sulphuric acid, and lastly, 10 drops of the nitrous solution. The stopper is then replaced, and the whole well shaken, set aside to allow the carbon disulphide to settle, and the supernatant liquid poured into another clean flask. The carbon disulphide is then treated three or four times successively with water in the same way till the free acid is mostly removed, the washings being all mixed in one flask; 10 c.c. of disulphide are then added to the washings, well shaken, and if at all coloured, the same process of washing is carried on. Finally, the two quantities of disulphide are brought upon a moistened filter, washed till free from acid, a hole made in the filter, and the disulphide which now contains all the iodine in solution allowed to run into a clean small flask, 30 c.c. of the sodium bicarbonate solution added, then brought under the thiosulphate burette, and the solution allowed to flow into the mixture while shaking until the violet colour is entirely discharged. The quantity so used represents the weight of iodine contained in 50 c.c. of the standard potassium iodide, and may be used on that basis to ascertain any unknown weight contained in a similar solution.

When very small quantities of iodine are to be titrated, weaker solutions and smaller vessels may be used.

This process is especially useful in determining small amounts of iodine in the presence of chlorine and bromine, as in mineral waters.

7. By ${}^{N}/_{10}$ Silver Solution and Starch Iodide (Pisani).

The details of this process are given under the head of silver assay and are of course simply a reversal of the method there given. This method is exceedingly serviceable for determining small quantities of combined iodine in the presence of chlorides and bromides, inasmuch as the silver solution does not react upon these bodies until the blue colour is destroyed.

IRON.

$Fe = 55{\cdot}85$.

Factors.

1 c.c. $^{N}/_{10}$ permanganate, dichromate or thiosulphate	$= 0{\cdot}005585$ Fe
,, ,, ,,	$= 0{\cdot}007185$ FeO
,, ,, ,,	$= 0{\cdot}007985$ Fe_2O_3

DETERMINATION IN THE FERROUS STATE.

1. Verification of the standard solutions of Permanganate or Dichromate.

THE determination of iron in the ferrous state has already been incidentally described under Analysis by Oxidation and Reduction, pp. 122 and 126. The present and following sections are an amplification of the methods there given, as applied more distinctly to ores and products of iron manufacture; but before applying the permanganate or dichromate process to these substances, and since many operators prefer, with reason, to standardize such solutions upon metallic iron, especially for use in iron analysis, the best method is given on p. 122. The apparatus used is shown in fig. 44.

Instead of the two flasks, many operators use a single flask, fitted with caoutchouc stopper, through which a straight glass tube is passed, fitted with an india-rubber slit valve (known as Bunsen's valve), which allows gas or vapour to pass out, but closes by atmospheric pressure when the evolution ceases.

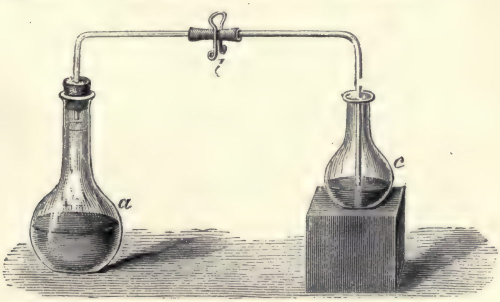


Fig. 44.

A large number of technical operators do not trouble themselves to arrange any apparatus of the kind described, but simply dissolve a weighed quantity of wire of known composition in a conical beaker covered with a clock glass or in a flask covered with a glass marble. If kept from draughts of cold air while dissolving so as to avoid convection, it is said that practically no oxidation takes place. The following plan answers well :—

Put into a 220 c.c. flask 25 c.c. of water and heat on a hot plate

till boiling. Then drop in the weighed portion (about 0·25 gm.) of iron wire and immediately add 15 c.c. of strong HCl and cover the flask with a glass marble. In 4-6 minutes the wire will have dissolved to a perfectly colourless solution, which should then be rinsed out into a basin and the titration with dichromate at once proceeded with.

The double iron salt (p. 123) is a very convenient material for adjusting standard solutions, but it must be most carefully made from pure materials, dried perfectly in the granular form, and kept from the light in small dry bottles, well closed.

It should be borne in mind that ferrous compounds are much more stable in sulphuric than in hydrochloric acid solution, and whenever possible sulphuric acid should be used as the solvent. When hydrochloric acid must be used, and permanganate is employed, some manganous or ammonium sulphate should be added unless the solution is very dilute.

Friend* finds that accuracy is attained, provided that the manganous sulphate present is not less than 2 gm. in 200 c.c., if (1) the titration is performed slowly with constant shaking, (2) the concentration of the HCl does not exceed $^N/_4$.

Jones and Jeffery† recommend a modified Zimmermann-Reinhardt process of titration in which the following reagents are employed :—

Manganese Solution : Prepared, according to Reinhardt's formula, by dissolving 200 gm. of crystallized manganese sulphate in 1000 c.c. of water, and adding to this a cooled mixture of 400 c.c. of concentrated sulphuric acid, 600 c.c. of water, and 1000 c.c. of phosphoric acid of sp. gr. 1·3. Stannous chloride : 50 gm. of the crystallized salt and 100 c.c. of concentrated hydrochloric acid made up to 1000 c.c. with water.

Mercuric chloride : A cold, saturated solution. Hydrochloric acid : Acid of sp. gr. 1·1. The slight oxidizing power sometimes possessed by the manganese solution, when freshly prepared, may be easily determined and allowed for if necessary ; but it has been found that this oxidizing effect is unmeasurable when the solution is a weak old. In the presence of hydrochloric acid, permanganate titrations give results which are a little too high, even when the manganese solution is employed ; the authors find that the small error so introduced is a constant one, independent of the amount present, and therefore easily allowed for. The titration is carried out as follows :—

The iron solution (in hydrochloric acid of 1·1 sp. gr.) is reduced with the smallest possible excess of stannous chloride, and 10 c.c. of mercuric chloride are added to the cold solution, the mixture being then allowed to stand for ten minutes to ensure the complete conversion of the stannous salt to the stannic condition, no appreciable oxidation of the reduced iron occurring in the meantime. A quantity of water, which may vary between 400 and 1000 c.c. without appreciable effect on the titration, is then mixed, in a capacious bowl, with a volume of the manganese solution equal to that of the hydrochloric acid present in the assay, and the mixture tinted with permanganate, of which one drop should suffice. The ferrous solution is then transferred to the bowl, together with the rinsings of its containing vessel, and the permanganate added, drop by drop, with constant stirring, until the end point is reached. 0·1 c.c. is then deducted from the burette reading, and the amount of iron present is calculated by reference to the known titre of the permanganate, as determined by titration against a ferrous solution free from hydrochloric acid.

* *Chem. Soc. Trans.*, 1909, **95**, 1228.

† *Analyst*, 1909, **34**, 306. See also note p. 124.

2. Reduction of Ferric Compounds to the Ferrous State.

This may be accomplished by metallic zinc or magnesium, for use with permanganate, or by stannous chloride or an alkali sulphite for dichromate solution. The magnesium method is elegant and rapid, but costly. In the case of zinc being used, the metal must either be free from iron or, if it contain any, the exact quantity must be known and allowed for; and further, the pieces of zinc used must be entirely dissolved before the solution is titrated.* The solution to be reduced by zinc should not contain more than 0·15 gm. Fe per 250 c.c., and for this quantity about 10 gm. of Zn and 25 c.c. H_2SO_4 are advisable; when the zinc is all dissolved, the whole should be boiled with exclusion of air, then cooled rapidly before titration with the permanganate. In the case of stannous chloride the solution must be clear, and is best made to contain 10 to 15 gm. per litre, as directed on p. 128. The point of exact reduction in the boiling hot and somewhat concentrated acid liquid may be known very closely by the discharge of colour in the ferric solution; but may be made sure by the use of a saturated aqueous solution of mercuric chloride as mentioned on p. 127.

It is exceedingly difficult to hit the exact point of reduction so that there shall be neither excess of tin nor unreduced iron, and technical iron analysts now almost universally use mercuric chloride as a precaution against excess of tin solution. The general method of procedure is to dissolve the material in diluted hydrochloric acid (1 acid 2 water) in a conical beaker moderately heated over a rose burner; when solution is complete the sides of the vessel are washed down with hot water, the liquid brought to gentle boiling, and strong tin solution added from a dropping bottle until the colour of the iron solution is nearly discharged, a dilute tin solution is then dropped in until all colour has disappeared, and there is a decided slight excess of tin. Cold air-free water is then washed over the sides of the beaker, the vessel covered with a clock glass placed in a bowl of cold water and allowed to cool, and a slight excess of the mercuric solution is then added, and the titration with dichromate is at once completed in the usual way (see pp. 126-128).

Some technical operators prefer to use sodium sulphite or ammonium bisulphite for the reduction. If sodium sulphite be used, the solution of iron must not be too acid and should be dilute, say a volume of half a litre for ½ gm. of Fe. The sulphite is added and the flask gently heated till the liquid is colourless. It is then boiled briskly till all SO_2 is dissipated; when cooled it is ready for titration with dichromate. In the case of ores containing titanium it is preferable to avoid the use of zinc for reduction, as it also reduces the titanium more or less; alkali sulphite does not.

The procedure with ammonium bisulphite is as follows:—† To the acid solution

*Beebe (*C. N.* **53**, 269) suggests the following convenient arrangement:—A strip of thin platinum foil, 1 in. square, is perforated all over with pin holes, then bent into a U form, and the ends connected with platinum wire so as to form a basket. In this is placed a piece of amalgamated zinc and the whole suspended by a stout platinum wire in the reducing flask. When lowered into the solution, another strip of platinum foil, 2 in. square, is dropped in and leaned against the wire carrying the basket; a very free evolution of hydrogen is then obtained from the foil. When the reduction is complete, the basket is lifted out and well washed into the beaker containing the liquid to be treated. C. Jones's reductor is often used, as described on page 234. Another method with zinc dust is shown on the next page.

† Austen, *C. N.* **46**, 287.

of the ore or metal, diluted and filtered, ammonia is added until a faint precipitate of ferric hydroxide is produced. This is re-dissolved with a few drops of HCl, and some strong solution of bisulphite added, in the proportion of about 1 c.c. for each 0·1 gm. of ore, or 0·05 gm. Fe. The mixture is well stirred, boiling water added, then acidified with dilute sulphuric acid, and boiled for half an hour: it is then ready for titration.

D. J. Carnegie* points out the value of zinc dust for the rapid reduction of ferric solutions, and suggests the following method of carrying it out.

The bottom of a dry and narrow beaker is covered with zinc dust sifted through muslin. A known volume of ferric solution, previously nearly neutralized with ammonia, is placed in the beaker and shaken with the zinc dust; then a known volume of dilute sulphuric acid is added and shaken for a few moments. The reduction is much more rapid in neutral than in acid solutions, but of course acid in this case must be present in excess to keep the iron in solution. Carnegie withdraws a portion of the reduced solution from the undissolved zinc by help of a filter, such as is described on p. 19, and, as measured volumes have been used, an aliquot part taken with a pipette may be at once titrated, and the amount of iron found.†

Clemens Jones‡ in a paper read before the American Institute of Mining Engineers, adopts the plan suggested by Carnegie, and has designed a special apparatus for filtering the ferric solution through a column of zinc dust. This arrangement gives complete reduction in a very short period of time, and is serviceable where a large number of titrations have to be carried on.

DETERMINATION OF IRON IN THE FERRIC STATE.

1. Direct Titration of Iron by Stannous Chloride (see p. 127).

2. Direct Titration of Iron by Titanous Chloride.

Titanous chloride ($TiCl_3$), which was employed in the first place as a reducing agent for the determination of ferric iron, has lately received much wider application in the domain of volumetric analysis, it being now successfully used for the quantitative determination of nitro-compounds, the azo-dyes and dyestuffs, etc.||

The readily oxidizable solution of titanous chloride is prepared and stored as follows:—

50 c.c. commercial titanous chloride (20 % solution) and 100 c.c. conc. HCl are boiled together in a small flask for about a minute, the mixture is cooled, made up to about $2\frac{1}{4}$ litres, thoroughly mixed by shaking, and the storage bottle A (see fig. 45) filled up to the neck with the solution.

* *J. C. S.* **53**, 468.

† Commercial zinc dust is probably a by-product in zinc manufacture, and cannot therefore be obtained pure. Samples examined by myself, and apparently by others also, do not, however, contain much iron, but a good deal of zinc oxide, with traces of cadmium and lead. Carnegie states that the oxide may be removed by repeatedly digesting with weak acid, or better still, by treatment with ammonium chloride and ammonia, the well-washed dust being finally dried on porous tiles in a vacuum. I find that by washing once with strong alcohol after the water and finally with ether, the dust may be rapidly dried in good condition, and when a quantity of such purified dust is obtained, the amount of iron in it may easily be determined once for all, and allowed for in titration. Good zinc dust is undoubtedly a valuable reagent in a laboratory for other purposes besides iron titrations.

‡ *C. N.* **60**, 93.

|| See Knecht and Hibbert "New Reduction Methods in Volumetric Analysis," 1910.

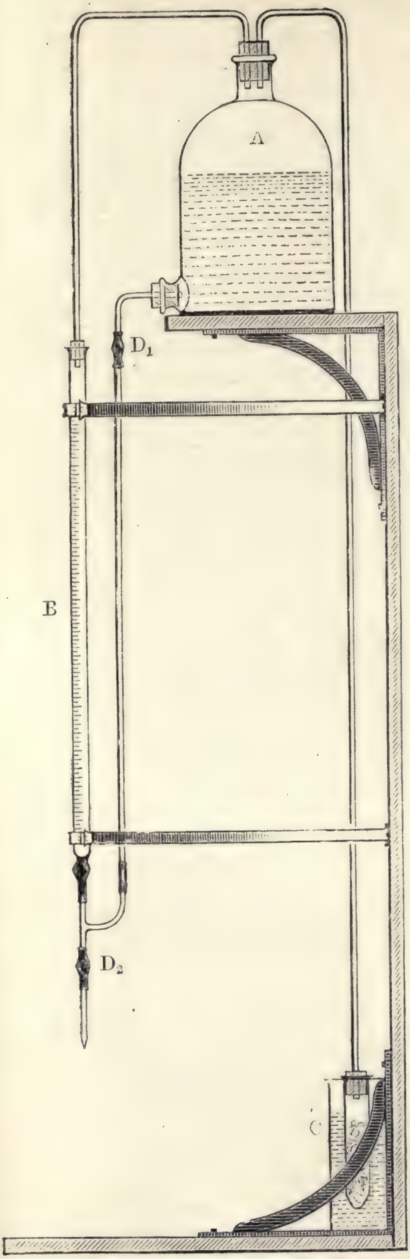


Fig. 45.

The mode of connection of this bottle with the burette (B) will readily be seen by the fig. 45. Rubber stoppers are used and at D_1 and D_2 are valves constructed of glass rod and rubber tubing as described on p. 13. C is a hydrogen generator consisting of a glass cylinder half filled with dilute HCl (1 : 1) into which dips an inner tube contracted at the bottom to a narrow aperture and filled with ordinary granulated zinc. The hydrogen generated when D_2 is opened passes into the storage bottle and burette. By opening the valve D_1 the titanous chloride flows into the burette and rises into the tube above it, then by opening D_2 the solution is entirely run out and the hydrogen allowed to escape for some minutes. The burette can now be filled up to the zero mark and the apparatus is ready for use.

Standardization of the Solution. Dissolve 3·511 gm. of the purest ferrous ammonium sulphate in water, add about 100 c.c. 5 $N.H_2SO_4$, and make up the solution to 250 c.c. in a measuring flask. Pipette 25 c.c. (=0·05 gm. Fe) of the well mixed solution into a flask and carefully oxidize with permanganate of about $^N/_{50}$ strength until a faint pink tinge is obtained. Then add a **large excess*** of potassium sulphocyanate and run in the titanous chloride from the burette until the

* A large excess renders the end-reaction much sharper.

red colour, due to ferric sulphocyanate, has entirely disappeared. Suppose for example that 25 c.c. of the iron solution, after oxidation, require 26·3 c.c. titanous chloride to reduce it, then

$$1 \text{ c.c. Ti } Cl_3 = 0{\cdot}0019 \text{ gm. Fe.}$$

Solutions of ferric iron, to which an excess of potassium sulphocyanate is added as indicator, can be titrated directly with the titanous solution. It is immaterial whether the iron is present in sulphuric or hydrochloric acid solution, but the presence of some mineral acid is essential, as otherwise the indicator is not sensitive. Ferrous iron must first be oxidized to the ferric state. This is generally done as follows :—

To a measured volume of the solution add ammonia and hydrogen peroxide, and remove the excess of oxygen by boiling the liquid for 5 to 10 minutes. Then add HCl in quantity more than sufficient to dissolve the ferric hydrate ; or :

To the ferrous solution add a crystal of $KClO_3$ and some HCl, boil down to a small bulk, add water or HCl, again evaporate down, and when the excess of chlorine has thus been removed the solution is ready for titration.

The reaction which takes place is

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4.$$

3. Titration by Sodium Thiosulphate.

Scherer first suggested the direct titration of iron with thiosulphate, which latter was added to a solution of ferric chloride until no further violet colour was produced. This was found by many to be inexact ; but Kremer* has made a series of practical experiments, the result of which is that the following modified method can be recommended.

The reaction which takes place is such as to produce ferrous chloride, sodium tetrathionate, and chloride. $2Na_2S_2O_3 + Fe_2Cl_6 + 2HCl = H_2S_4O_6 + 4NaCl + 2FeCl_2$. The thiosulphate, which may conveniently be of $^N/_{10}$ strength, is added in excess, and the excess determined by iodine and starch.

Method of Procedure : The iron solution, containing not more than 1 per cent. of metal, which must exist in the ferric state without any excess of oxidizing material (best obtained by adding excess of hydrogen peroxide, then boiling till the excess is expelled), is moderately acidified with hydrochloric acid, sodium acetate added till the mixture is red, then dilute hydrochloric acid until the red colour disappears ; then diluted till the iron amounts to $\frac{1}{2}$ or $\frac{1}{4}$ per cent., and $^N/_{10}$ thiosulphate added in excess, best known by throwing in a particle of potassium sulphocyanide after the violet colour produced has disappeared ; if any red colour appears, more thiosulphate must be added. Starch and $^N/_{10}$ iodine are then used to ascertain the excess. A mean of several experiments gave 100·06 Fe, instead of 100.

J. T. Norton † has carefully experimented on this method and

* *Journ. f. Pract. Chem.* **84**, 339. † *J. Am. C. S.* 1899, p. 25.

found that it needs careful management to ensure accurate results. The volume of dilution and amount of acid must be carefully regulated, so also must the amount of thiosulphate used in excess. There should always be at least 15 c.c. of thiosulphate in excess with 0·1 gm. of ferric oxide and 1 c.c. of strong hydrochloric acid in not less than 400 or 500 c.c. of freshly boiled water used for dilution. The time occupied in reduction should be as short as possible.

METHOD OF PROCEDURE: In treating ferric oxide, the following method is recommended:—Dissolve an amount not exceeding 0·2 gm. of the oxide in 2 c.c. of hydrochloric acid, evaporate to a pasty mass, dilute to about 800 c.c. with freshly-boiled water, add a drop of potassium sulphocyanide, and into this solution run 50 c.c. of $^N/_{10}$ sodium thiosulphate; allow the liquid to stand until perfectly colourless, and determine the excess of thiosulphate by $^N/_{10}$ iodine and starch. For quantities of iron oxide up to 0·2 gm. this process is quick and most accurate; when care is taken to preserve the relations of acidity and dilution, twice the amount of ferric oxide mentioned above may be handled.

The accuracy of the process is not interfered with by the presence of salts of the alkalies, strontia, lime, magnesia, alumina, or manganous oxide; neither do salts of nickel, cobalt, or copper, unless their quantity is such as to give colour to the solution.

The process is a rapid one, and with care gives very satisfactory results.

4. Determination with Iodine and Sodium Thiosulphate.

When ferric chloride is digested with potassium iodide in excess, iodine is liberated, which dissolves in the free potassium iodide—

$$FeCl_3 + KI = FeCl_2 + KCl + I.$$

METHOD OF PROCEDURE: The hydrochloric acid solution, which must contain no free chlorine or nitric acid, and all the iron in the ferric state, is nearly neutralized with caustic potash or soda, transferred to a well-stoppered flask, and an excess of strong solution of potassium iodide added; it is then heated to 50° or 60° C. on the water bath, closely stoppered, for about twenty minutes; the flask is then cooled, starch added, and titrated with thiosulphate till the blue colour disappears. This process gives very satisfactory results in the absence of all substances liable to affect the potassium iodide, such as free chlorine or nitric acid, and is particularly serviceable for determining small quantities of iron.

Instead of starch another indicator is suggested by Haswell.* To an aliquot portion of the solution of the ferric salt a little cupric sulphate and salicylic acid are added as an indicator, and then from a burette standard thiosulphate solution is run in until the violet coloration is entirely destroyed. The liquid is then titrated back with the solution of the ferric salt, until the colour just reappears.

Joseph† has shown that good results may be obtained by the following simplified procedure:—

To the ferric solution, acidified with HCl (the quantity used seems to be of no practical importance), add a few grams of KI, and at once titrate the iodine liberated with $^N/_{10}$ thiosulphate. In those frequent cases where the substance

* *Zeits. f. angew. Chem.* **49**, 1265. † *J. S. C. I.*, 1910, **29**, 187.

must be dissolved in HCl and potassium chlorate, on account of the presence of ferrous iron, the liquid is boiled almost to dryness before titration.

1 c.c. $^N/_{10}$ thiosulphate $=0{\cdot}005585$ gm. Fe.

The solution is standardized either with iodine or with iron alum. Excellent results are recorded.

5. Determination of Iron by Colorimetric Methods.

These methods, which approach in delicacy the Nessler test for ammonia, are applicable for very minute quantities of iron, such as may occur in the ash of bread when testing for alum, water residues, alloys, and similar cases.

It is first necessary to have a standard solution of iron in the ferric state, which can be made by dissolving 1·004 gm. of iron wire in nitro-hydrochloric acid, precipitating with ammonia, washing and re-dissolving the ferric oxide in a little hydrochloric acid, then diluting to one litre. 1 c.c. of this solution contains 1 milligram of pure iron in the form of ferric chloride. It may be further diluted, when required, so as to contain $\frac{1}{10}$ milligram in a c.c., and this is the best standard to use.* The solution for producing the colour is either potassium ferrocyanide or thiocyanate dissolved in water (1 : 20).

PROCEDURE WITH FERROCYANIDE: The material containing a minute unknown quantity of iron, say a water residue, is dissolved in hydrochloric acid, and diluted to 100 c.c., or any other convenient measure. 10 c.c. are measured into a white glass cylinder marked at 100 c.c., 1 c.c. of concentrated nitric acid added (the presence of free acid is always necessary in this process), then diluted to the mark with distilled water, and well stirred.

1 c.c. of ferrocyanide solution is then added, well mixed, and allowed to stand at rest a few minutes to develop the colour.

A similar cylinder is then filled with a mixture of say, 1 c.c. of standard iron solution, 1 c.c. nitric acid and distilled water, and 1 c.c. ferrocyanide added; if this does not approach the colour of the first mixture, other quantities of iron are tried until an exact similarity of colour occurs. The final adjustment is made by pouring out a little of the stronger solution into a measuring cylinder until the tints are exactly equal. The calculation is made exactly as in Nesslerization. The exact strength of the iron solution being known, it is easy to arrive at the quantity of pure iron present in the substance examined, and to convert it into its state of combination by calculation.

Carter Bell† adopts the following plan in the case of waters:— 70 c.c. of the water are evaporated to dryness in a platinum dish, and gently ignited to burn off organic matters. 1 c.c. of dilute nitric acid (50 c.c. of strong acid in a litre) is then poured over the residue from a pipette, and evaporated to dryness on the water bath; the residue is then dissolved in 1 c.c. of a 10 per cent. hydrochloric acid, 5 or 10 c.c. of distilled water added, the solution filtered through a small filter, washed, made up to 50 c.c. in a Nessler glass, and finally mixed with 1 c.c. each of ferrocyanide solution and nitric acid.

* A solution of this strength can also be made by weighing 0·7022 gm. of pure ferrous ammonium-sulphate (p. 123), dissolving in water, acidifying with sulphuric acid, adding sufficient permanganate solution to convert the iron exactly into ferric salt, then diluting to 1 litre. Hydrogen peroxide may also be used in place of permanganate, taking care to dissipate the excess by boiling.

† *J. S. C. I.* **8**, 175.

With Thiocyanate.—Thomson* recommends this method as being specially available in the presence of other ordinary metals and organic matters, silver, copper, and cobalt being the only interfering substances. The delicacy is said to be such that 1 part of iron can be recognised in 50 million parts of water. The presence of free mineral acids adds greatly to the sensitiveness. The standard ferric solution may be the same as for ferrocyanide; and in preparing the material for titration the weighed quantity is dissolved in an appropriate acid, evaporated nearly to dryness, taken up with water, converted into the ferric state by cautious addition of permanganate, then diluted with water to a measured volume, and an aliquot portion taken for titration.

The standard iron solution used by Thomson=$\frac{1}{10}$ mgm. Fe per c.c. (0·7022 gm. double iron salt [oxidized] per litre.)

EXAMPLE: Into two colourless glass cylinders marked at 100 c.c. pour 5 c.c. of nitric or hydrochloric acid (1 : 5), together with 15 c.c. of dilute thiocyanate, and to one glass a measured volume of the solution to be tested; fill up both glasses to the mark with pure water. If iron be present, a blood red colour more or less intense will be produced. Standard iron is then cautiously added from a burette to the other glass till the colour agrees. The quantity of Fe taken should not require more than 2 or 3 c.c. of the standard to equal it, or the colour will be too deep for comparison.

If other metals are present which forms two sets of salts, they must be in the higher state of oxidation, or the colour is destroyed. Oxalic acid also destroys it. Examples in the presence of a great variety of metals show very good results.

IRON ORES, IRON AND STEEL.

THE great desideratum in the analysis of iron ores is to get them into the finest possible state of division, and ten minutes' hard work with the agate mortar will often save hours of treatment of the material with acids. The operator of experience can generally tell if the ore to be examined will dissolve in acids. Some clay ironstones and brown hæmatites contain organic matters, and they are best first roasted in an open platinum crucible, gradually raising the heat to redness; this course is advisable also when an ore contains pyrites; this latter is easily converted to Fe_2O_3 by roasting. The proportion in iron ores is generally under half a per cent. Some ores give a residue in any case by treatment with HCl; this should be separated by filtration and fused with fusion mixture, which will render all the iron in a soluble state. In the analysis of iron ores it is very often necessary to determine not only the total amount of iron, but also the state in which it exists; for instance, magnetic iron ore consists of a mixture of the two oxides in tolerably definite proportions, and it is sometimes advisable to know the quantities of each.

In order to prevent, therefore, in such cases, the further oxidation

* *J. C. S.* 1885, 493.

of the ferrous oxide, the little flask apparatus (fig. 46) adopted by Mohr is recommended, or that shown in fig. 44 is equally serviceable.

The left-hand flask contains the weighed ore in a finely powdered state, to which tolerably strong hydrochloric acid is added; the other flask contains distilled water only, the tube from the first flask reaching to the bottom of the second. When the ore is ready in the flask and the tubes fitted, hydrochloric acid is poured in, and a few grains of sodium bicarbonate added to produce an evolution of CO_2. The air of the flask is thus expelled, and as the acid dissolves the ore, the gases evolved drive out in turn the CO_2, which is partly absorbed by the water in the second flask. When the ore is all dissolved, the lamp is removed, and the water immediately rushes out of the second flask into the first, diluting and cooling the solution of ore, so that, in the majority of cases, it is ready for immediate titration. If not sufficiently cool or dilute, a sufficient quantity of boiled and cooled distilled water is added.

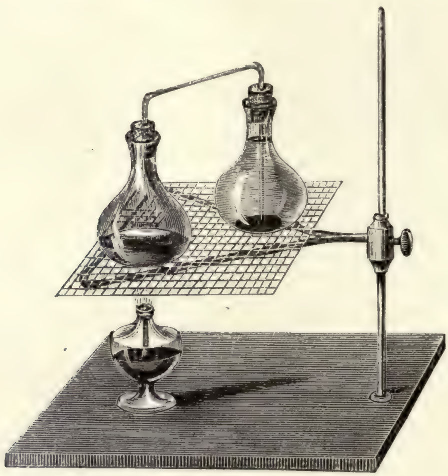


Fig. 46.

When the total amount of iron present in any sample of ore has to be determined, it is necessary to reduce any peroxide present to the state of protoxide previous to titration.

Reduction to the Ferrous state may be effected by sodium sulphite in dilute solution, but not so with stannous chloride; the latter must be used in a boiling and concentrated solution strongly acidified with hydrochloric acid. Most technical operators now use the tin method, which, by the help of mercuric chloride as described on p. 127, is rendered both rapid and trustworthy. With both the sulphite and the tin methods, dichromate is the titrating solution invariably used. When permanganate is to be used for titration, the reduction is always best made with zinc or magnesium in sulphuric or very weak hydrochloric acid solution. With dichromate, the best reducing agent is either pure sodium sulphite, ammonium bisulphite, or stannous chloride.

1. Red and Brown Hæmatites.—Red hæmatite consists generally of ferric oxide accompanied with matters insoluble in acids. Sometimes, however, it contains phosphoric acid, manganese, and earthy carbonates.

Brown hæmatite contains hydrated ferric oxide, often accompanied by small quantities of ferrous oxide, manganese, and alumina; sometimes traces of copper, zinc, nickel, cobalt, with lime, magnesia, and silica; occasionally also organic matters.

In cases where the total iron only has to be determined, it is advisable to ignite gently (about 0·5 gm.) to destroy organic matters, then treat with strong hydrochloric acid at near boiling heat till all iron is dissolved, and in case ferrous oxide is present add small quantities of potassium chlorate, afterwards evaporating to dryness to dissipate free chlorine; then dissolve the iron with hot dilute hydrochloric acid, filter, and make up to a given measure for reduction and titration.

In some instances the insoluble residue persistently retains some iron in an insoluble form; when this occurs, resort must be had to fusing the residue with fusion mixture, followed by solution in hydrochloric acid.

2. Magnetic Iron Ore.—The ferrous oxide is determined first by means of the apparatus fig. 44 or 46. The ore (about 1 gm.) is put into the vessel in a state of very fine powder, strong hydrochloric acid added, together with a few grains of sodium bicarbonate, and heat applied gently until the ore is dissolved, then diluted if necessary, and titrated with dichromate or permanganate. Technical operators generally use only a covered beaker or a flask closed with a glass marble.

3. Spathose Iron Ore.—The total amount of ferrous oxide in this carbonate is ascertained directly by solution in hydrochloric acid; as the carbonic acid evolved is generally sufficient to expel all air, the tube dipping under water may be dispensed with. If the ore contains pyrites it should be first roasted, but this of course converts the ferrous carbonate into Fe_2O_3.

As the ore contains, in most cases, the carbonates of manganese, lime, and magnesia, these may all be determined, together with the iron, as follows:—

A weighed portion of ore (about 1 gm.) is brought into solution in hydrochloric acid, after ignition if pyrites is present, and filtered, if necessary, to separate insoluble silicious matter.

The solution is then boiled with a few drops of nitric acid to peroxidize the iron, diluted, nearly neutralized with ammonia, and a solution of ammonium acetate added, then boiled for two minutes and allowed to settle. The precipitate is collected on a filter and washed with boiling water containing a little ammonium acetate. It is then dissolved off the filter in HCl, which also dissolves any Al_2O_3 or P_2O_5 which may be present. The liquid is then evaporated, reduced, and titrated as usual.

The filtrate from the above is concentrated by evaporation, cooled, 3 or 4 c.c. of bromine added, and well mixed by shaking; when most of the bromine is

dissolved the liquid is rendered alkaline by ammonia, and gently warmed till the Mn separates in large flocks as hydrated oxide, which is collected and titrated by one of the methods given under "Manganese."

The filtrate from the last is mixed with ammonium oxalate to precipitate the lime, which is determined by permanganate, as on p. 172.

The filtrate from the lime contains the magnesia, which may be precipitated with sodium phosphate and ammonia, and the precipitate weighed as usual, or titrated with uranium solution.

4. Determination of Iron in Silicates.—Wilbur and Whittlesey* give a series of determinations of iron existing in various silicates, either as mixtures of ferric and ferrous salts or of either separately, which appear very satisfactory.

The very finely powdered silicate is mixed with rather more than its own weight of powdered fluor-spar or cryolite (free from iron) in a platinum crucible, covered with hydrochloric acid, and heated on the water-bath until the silicate is all dissolved. During the digestion either carbonic acid gas or coal gas free from H_2S is supplied over the surface of the liquid so as to prevent access of air. When decomposition is complete (the time varying with the nature of the material), the mixture is diluted and titrated with permanganate in the usual way for ferrous oxide; the ferric oxide can then be reduced by zinc and its proportion found.

By Hydrofluoric Acid.—Silicates may also be decomposed by hydrofluoric acid, about 2 gm. being treated with 40 c.c. of the acid (containing about 20 per cent. HF) in a deep platinum crucible. In this case Leeds† recommends that the finely powdered silicate be mixed with a suitable quantity of dilute sulphuric acid, and air excluded by CO_2 during the action of the hydrofluoric acid, which should be aided by heat. When decomposition is complete, the crucible and its contents are quickly cooled, diluted with recently boiled water, and the ferrous salt determined with permanganate or dichromate as usual.

If the hydrofluoric acid has been prepared in leaden vessels, it invariably contains SO_2; in such cases it is necessary to add to it, previous to use, some hydrogen peroxide (avoiding excess) so as to oxidize the SO_2.

The process is a rapid and satisfactory one, yielding much more accurate results than the method of fusion with alkali carbonates or acid potassium sulphate.

5. Colorimetric determination of Carbon in Steel and Iron.—The method devised by Eggertz, and largely adopted by chemists for determination of combined carbon, is well known, but is open to the objection that minute quantities of carbon cannot be discriminated by it, owing to the colour of the ferric nitrate present. Stead‡ in order to overcome this difficulty has devised a method described as follows:—

In some careful investigations on the nature of the colouring matter which is produced by the action of dilute nitric acid upon white iron and steel, it was found it had the property of being

* *C. N.* **22**, 2. † *Z. a C.* **16**, 323. ‡ *C. N.* **47**, 285.

soluble in potash and soda solutions, and that the alkaline solution had about two and a half times the depth of colour possessed by the acid solution. This being so, it was clear that the colouring matter might readily be separated from the iron, and be obtained in an alkaline solution, by simply adding an excess of sodium hydrate to the nitric acid solution of iron, and that the colouring solution thus obtained might be used as a means of determining the amount of carbon present. Upon trial this was found to be the case, and that as small a quantity as 0·03 per cent. of carbon could readily be determined.

The solutions required are :—
Nitric acid, 1·20 sp. gr.
Sodium hydroxide, solution 1·27 sp. gr.

METHOD OF PROCEDURE : One gm. of the steel or iron to be tested is weighed and placed in a 200 c.c. beaker, and after covering with a watch-glass, 12 c.c. of standard nitric acid are added. The beaker and contents are then placed on a warm plate, heated to about 90° to 100° C., and there allowed to remain until dissolved, which does not usually take more than ten minutes. At the same time a standard iron containing a known quantity of carbon is treated in exactly the same way, and when both are dissolved 30 c.c. of hot water are added to each and 13 c.c. soda solution.

The contents are now to be well shaken, and then poured into a glass measuring jar and diluted till they occupy a bulk of 60 c.c. After again well mixing and allowing to stand for ten minutes in a warm place, they are filtered through dry filters, and the filtrates, only a portion of which is used, are compared. This may be done by pouring the two liquids into two separate measuring tubes in such quantity or proportion that upon looking down the tubes the colours appears to be equal.

Thus if 50 measures of the standard solution are poured into one tube, and if the steel to be tested contains say half as much as the standard, there will be 100 measures of its colour solution required to give the same tint. The carbon is therefore inversely proportional to the bulk compared with the standard, and in the above assumed case, if the standard steel contained 0·05 per cent. carbon, the following simple equation would give the carbon in the sample tested :—

$$\frac{0{\cdot}05 \times 50}{100} = 0{\cdot}025 \text{ per cent.}$$

The proportions here given must be strictly adhered to in order to ensure exactness. The colours from low carbon irons differ in tint from those in high carbon steels, and therefore a low standard specimen must be used for comparison. It is evident that the safest plan to ensure absolute comparison is to weigh and dissolve a known standard steel or iron for each batch of tests.

Stead has devised a special colorimeter for the process, but it is evident that any of the usual instruments may be used.

Arnold* gives the following conditions as necessary for the accurate working of the Eggertz test :—

(*a*) The standard steel should have been made by the same process as the sample.

(*b*) The standard should be in the same physical condition, as far as this can be secured by mechanical means.

(*c*) The standard should not differ greatly in the percentage of carbon.

* *Steel Works Analysis*, p. 46.

(*d*) The solution of the standard and the samples should be made at the same time, and under identical conditions, and the comparisons should be made without delay.

(*e*) Above all, the standard should be above suspicion, its carbon contents having been settled on the mean of several concordant combustions made on different weights of steel from a homogeneous bar.

6. Determination of Phosphorus in Iron and Steel.—Dudley and Pease* adopt the following method :—

1 gm. of the sample is dissolved in an Erlenmeyer flask, in 75 c.c. of nitric acid of sp. gr. 1·15 : when dissolved, it is boiled for a minute and mixed with 10 c.c. of a solution of potassium permanganate, and then again boiled until manganese dioxide begins to separate. The liquid is now cleared by the cautious addition of pure ferrous sulphate ; heated to 85° C., and mixed with 75 c.c. of ammonium molybdate solution at 27° C. After shaking for five minutes in a whirling apparatus, the precipitate is washed with solution of ammonium sulphate until the washings give no colouration with ammonium sulphide, and then dissolved in a mixture of 5 c.c. of ammonia and 25 c.c. of water. The solution is now mixed with 10 c.c. of strong sulphuric acid, diluted to 200 c.c. and reduced with zinc. The solution is then titrated with permanganate. The volume of the latter which represents I gm. of Fe equals 0·01724 gm. of P.

7. Determination of Sulphur in Iron and Steel.—J. Thill† gives the following method :—

METHOD OF PROCEDURE : By attacking the metal with hydrochloric acid in the well-known apparatus used for this purpose, the sulphur is liberated as sulphuretted hydrogen. The gas is received in 25 c.c. of a decinormal solution of arsenious acid, to which has been added 50 c.c. of a cold saturated solution of bicarbonate of soda. Care should be taken that the gas is not given off too rapidly.

When the attack is finished, the gas which still fills the apparatus is driven out by means of a current of carbonic acid, and the passage of this current of gas is continued until the hydrochloric acid carried with it has neutralized the alkaline solution, and precipitated almost the whole of the trisulphide of arsenic. This operation takes eight or ten minutes.

A few c.c. of hydrochloric acid are added, and the volume made up to 500 c.c. and filtered. The filtrate is collected in a dry beaker, and 100 c.c. are taken, and titrated with $^{N}/_{10}$ iodine, after adding starch and a sufficient quantity of ammonium carbonate to render the solution alkaline.

From the number of c.c. of iodine used is subtracted the number of c.c. required by 25 c.c. of a decinormal solution of arsenious acid. The difference corresponds to the sulphuretted hydrogen given off. This result, multiplied by 0·0024 gives the amount of sulphur contained in the sample.

At the National Physical Laboratory, Bushy House, Teddington, the volumetric determination of sulphur is carried out thus :—‡

The steel drillings are dissolved in an evolution flask in hydrochloric acid of 1·10 sp. gr. the operation being aided by heat, although boiling the acid should be avoided. Prior to the commencement of the operation, the evolution flask and entire apparatus are filled with an atmosphere of carbon dioxide, obtained by passing a stream of this gas, derived from a cylinder of liquid carbonic acid, through the entire apparatus. The evolved gases, aided towards the end of the operation by a further stream of CO_2 are bubbled through an absorption flask containing a solution of cadmium acetate strongly acidified with acetic acid (25 gm. pure cadmium acetate and 100 gm. glacial acetic acid per litre). After passing this flask

* *J. Anal. Chem.* **7**, 108. † *Z. a C.* **38**, 342.

‡ Rosenhain, Iron and Steel Institute Journal, Vol. I., 1908.

the gases pass through a narrow-bore tube of vitreous silica heated to redness by a Bunsen burner with a flat flame, the gases passing finally through a second cadmium acetate absorption flask and then away to the fume chamber. When the steel has completely dissolved, the contents of the two absorption flasks are mixed and the yellow cadmium sulphide is filtered off; this is a rapid operation since the flask need not be washed carefully,—the operation is merely intended to separate the sulphide from the bulk of the absorption liquid. As soon as this has been done the precipitate is washed from the filter back into the original flask, and there dissolved in 10 c.c. of standard iodine solution,* the action being aided by the addition of a small quantity of HCl. The excess of iodine is then titrated by means of sodium thiosulphate and starch. It is to be observed that while this titration can be carried out in the liquid of the absorption flasks without filtration, it has been found that this occasionally leads to discrepancies in the results. Apparently, particularly in the case of high carbon steel, the evolved gases carry into the absorption flask something which is capable of absorbing iodine, but which is not sulphur; this disturbing substance can be eliminated by the filtration described above. A table is given showing the comparative results obtained by this process and by the gravimetric (oxidation) method, the agreement in all cases being exceedingly close.

LEAD.

Pb = 207·1.

THE accurate determination of lead is in most cases better effected by weight than by measure; there are, however, instances in which the latter may be used with advantage. The precipitation as oxalate or carbonate is only of use where the lead exists in the form of a tolerably pure salt or metal.

1. As Oxalate (Hempel).—The acetic lead solution, which must contain no other body precipitable by oxalic acid, is put into a 300 c.c. flask, and a measured quantity of normal oxalic acid added in excess, the flask filled to the mark with water, shaken, and put aside to settle; 100 c.c. of the clear liquid may then be taken, acidified, with sulphuric acid, and titrated with permanganate for the excess of oxalic acid. The amount so found multiplied by 3, and deducted from that originally added, will give the quantity combined with the lead.

2. Alkalimetric Method (Mohr).—The lead is precipitated as carbonate by means of a slight excess of ammonium carbonate, together with free ammonia: the precipitate well washed, and dissolved in a measured excess of normal nitric acid: neutral solution of sodium sulphate is then added to precipitate the lead as sulphate. Without filtering, the excess of nitric acid is then determined by normal alkali, each c.c. combined being equal to 0·10355 gm. of lead.

3. Dichromate Method.—1 c.c. $^{N}/_{10}$ dichromate = ·010355 gm. Pb.

The following process for carbonate ores, pig lead, and specially for red and white leads and litharge, has been worked out by J. H. Wainwright†. The necessary solutions are: potassium dichromate, of such strength that 1 c.c. represents about 0·01 gm. of metallic lead, not much more or less, standardized either upon pure metal, or on white lead which has been accurately analysed for actual lead by weight: silver nitrate solution as outside indicator, not exceeding 2 or 3 per cent. in strength.

* 2 gm. of re-sublimed iodine are dissolved in 50 c.c. of water containing 4 gm. of KI, and diluted to 1 litre.

† *J. Am. C. S.* **19**, 389.

METHOD OF PROCEDURE: From 1 to 1·5 gm. of ore, litharge, etc., is dissolved in 10 to 15 c.c. of nitric acid (sp. gr. 1·20), the solution made slightly alkaline with ammonia, and a considerable excess of acetic acid added. It is then boiled, and potassium dichromate solution, in sufficient quantity to precipitate nearly all the lead, is run in from a burette. The liquid is boiled until the precipitate becomes orange-coloured, after which the titration is finished, the final point being indicated by contact with silver nitrate as an outside indicator on a white plate.

The precautions to be observed are:—

The solution of the lead salt must be as concentrated as possible, and decidedly acid with acetic acid. There must be absence of other metals, especially such as can exist in lower forms of oxidation. Antimony and tin, unless thoroughly oxidized, and bismuth are particularly to be avoided. During titration the solution should be kept as near the boiling-point as possible. The strength of the dichromate solution should not vary much from that given above, nor should the solution of silver nitrate.

In the case of dealing with ores containing small quantities of silver, it is desirable to precipitate this before filtration with a little solution of sodium chloride. In this case it is well to employ larger drops of the silver nitrate used as indicator.

The method is specially suitable for such substances as white lead, red lead, litharge, etc. Red lead is dissolved by treating it with nitric acid, and adding a dilute solution of oxalic acid drop by drop until the lead oxide is completely dissolved. If organic matter is present the solution should be filtered before titration. White lead can be dissolved directly in acetic acid, and the solution titrated without filtration. In the case of white lead ground in oil, the sample should be dissolved in dilute nitric acid, the solution boiled, filtered, ammonia added in excess, and then an excess of acetic acid. The method can also be used with ingot lead, and alloys containing tin and antimony, but the sample must be thoroughly oxidized by repeated evaporation with fuming nitric acid, and the solution filtered before titration.

The lead in solution, after addition of ammonium or sodium acetate, may be precipitated by excess of $^{N}/_{10}$ dichromate solution. After boiling for a minute or two the precipitate is quickly filtered off, well washed, and the excess of dichromate in the cooled filtrate titrated with standardized ferrous ammonium sulphate solution and potassium ferricyanide as external indicator. Or the excess of dichromate in the filtrate may be determined iodimetrically by addition of potassium iodide and titration with sodium thiosulphate.

Lead in various Ores.—An investigation of many methods of determining this metal has been carried out by J. C. Bull.* The best results, including the foregoing dichromate process, were obtained by the molybdate and the ferrocyanide methods. The initial procedure in all the trials was to separate the lead as sulphate, which contained also gangue and other insoluble sulphates, by treating the ore with nitric or nitro-hydrochloric acid, evaporating with sulphuric acid and filtering off from soluble sulphates after being diluted.

The Molybdate Method.—The mixture of lead sulphate and impurities, obtained as above, is boiled for at least ten minutes with ammonium acetate solution; the solution is then acidified with acetic acid, diluted to 200 c.c., again boiled, and a standard ammonium molybdate solution added until all the lead is precipitated. The end-point is ascertained by shaking the solution vigorously, allowing it to stand for a few minutes, and testing 1 drop of the clear liquid with 1 drop of a

* *Analyst*, **28**, 15.

solution of 1 part tannin in 300 parts water and 1 drop of a lead solution; the appearance of a yellow colour indicates the presence of ammonium molybdate in excess. The molybdate solution is prepared by dissolving 9 grammes of the salt in 1 litre of water and standardizing against lead sulphate. Since the indicator is not very sensitive, requiring about 0·8 c.c. of molybdate to affect it, a blank must be made to ascertain the correction due to this. This method gave very good results when tried on the ores; the presence of antimony, bismuth, and calcium had no effect on it; but in the presence of barium and, to a lesser extent, strontium, it gave low results.

The Ferrocyanide Method.—The mixture containing the lead sulphate is gently heated to boiling with 10 c.c. of a saturated solution of ammonium carbonate. After cooling, the precipitate is transferred to a filter, thoroughly washed, and then placed with the filter-paper in a flask containing a hot mixture of 5 c.c. glacial acetic acid and 25 c.c. water. This is boiled until the lead carbonate has dissolved, diluted to 150 c.c., heated to 60° C., and titrated with standard 1 per cent. potassium ferrocyanide solution, drops of uranium acetate solution placed on a white tile being used as indicator. Here also the correction due to the indicator must be determined. This method also gave very good results when no interfering metals were present.

4. Lead in Citric and Tartaric Acids, and in Cream of Tartar.—Warington* has worked out the best method of ascertaining the proportions of lead in these commercial acids, and shows that ammonium sulphydrate is to be preferred to sulphuretted hydrogen for the process, inasmuch as the tint produced is much more uniform throughout a long scale, and very free from turbidity. Warington's description of the method is as follows:—

The depth of tint produced for the same quantity of lead present is far greater in an ammoniacal tartrate or citrate solution than in the same volume of water; it is quite essential, therefore, if equality of tint is to be interpreted as equality of lead, that all comparisons should be between two citrate and tartrate solutions, and not between one of these and water.

To carry out the method it is necessary to have solutions of lead-free tartaric and citric acids supersaturated with pure ammonia; these solutions should develop no colour when treated with ammonium sulphydrate. A convenient strength is 100 gm. of acid in 300 c.c. of final solution.

The standard lead solutions are made by dissolving 1·6 gm. of crystallized lead nitrate dried over sulphuric acid in a litre of water, each c.c. = 0·001 gm. Pb. A weaker solution is also made by diluting 100 c.c. of this to a litre.

Of the tartaric or citric acid to be examined, 40 gm. are taken and dissolved in a little water; warm water is most convenient for crystal and cold for powder; the solution is best prepared in a flask. To the cold solution pure strong ammonia is gradually added till it is in slight excess; the final point is indicated in the case of tartaric acid by the solution of the acid ammonium tartrate first formed; in the case of citric acid it is conveniently shown by a fragment of turmeric paper floating in the liquid. When an excess of ammonia is reached the liquid is cooled, diluted to 120 c.c., and filtered.

As a preliminary experiment 10 c.c. are taken, diluted to 50 c.c. in the measuring cylinder, and placed in a Nesslerizing glass, one drop of ammonium sulphydrate solution added, and the whole well stirred; the colour developed indicates what volume of solution should be taken for the determination,—this volume may range from 5 c.c. to 50 c.c. If less than 50 c.c. are taken the volume is brought to 50 c.c. with water, and one drop of ammonium sulphydrate is then added.

The tint thus produced has now to be matched with the pure solutions. A volume of the pure ammoniacal tartrate or citrate, identical with that taken of the acid under examination, receives a measured quantity of lead solution from

* *J. S. C. I.* 1893, **12**, 97, 222.

the burette, the volume is brought to 50 c.c., it is placed in a Nesslerizing glass, and receives one drop of ammonium sulphydrate; the experiment is repeated till a match is obtained. As in the previous method, the best comparison of tints is obtained by making finally three simultaneous experiments, one with the acid under examination, the other two with pure acid containing slightly varying amounts of lead, the aim being that the tint given by the acid to be analysed shall lie within this narrow scale. In following this method, considerable use has to be made of the weaker of the two lead solutions already mentioned.

The whole time required for a determination of lead by this method now given is about 1½ hours: this time will be somewhat shortened as the operator becomes familiar with the tints produced by varying proportions of lead. If traces of copper or iron are present, any interference on their part may be removed by adding to the alkaline solution a few drops of potassium cyanide solution.

Tatlock and Thomson* proceed as follows :—

(1) Cream of Tartar.—Treat 10 grams with 50 c.c. of water and 40 c.c. of 2N ammonia solution, agitating till dissolved, then making up to 100 c.c. with water, mixing well and filtering through a dry filter.

(2) Tartaric acid.—Take 10 grams and use 81 c.c. of 2N ammonia solution and 9 c.c. of water, etc., as in (1).

(3) Citric acid.—Take 10 grams and use 85 c.c. of 2N ammonia solution and 5 c.c. of water, etc., as in (1).

Of the 100 c.c. of filtered liquid obtained as above, 50 c.c. are taken and to them are now added 0·1 gm. of KCy and 1 c.c. of a colourless or almost colourless strong solution of ammonium sulphide, and comparison then made with a standard solution of lead as described above. It is important to notice, however, that the amount of lead present in 50 c.c. of the standard solution, and also in the quantity of sample used, should not exceed 0·2 mgm. and that no lead should be added to make up deficiency after the addition of ammonium sulphide, but that a fresh standard should always be prepared. The reagents should invariably be added in the order mentioned.

Dr. Mac Fadden in a report to the Local Government Board † recommends the adoption of a limit of 0·002 per cent. (approximately 1/7th grain per lb.) of lead as impurity in tartaric and citric acids and cream of tartar.

5. Colorimetric determination for Waters.—When there is no other metal than lead present, simple addition of freshly made sulphuretted hydrogen water in the presence of weak acetic acid as suggested by Miller gives good results, comparison being made with a standard solution of lead acetate containing 0·1831 gm. per litre. Each c.c. = 0·0001 gm. lead. The determination is made in colourless glass cylinders in the same way as described for copper (p. 204), or iron (p. 238), taking care that the comparative tests are made under precisely the same conditions.

6. Colorimetric determination of lead in the presence of iron (for testing chemicals generally). J. M. Wilkie‡ recommends the following procedure :—

A weighed portion of the substance is dissolved in water and the solution made distinctly acid by adding a few drops of acetic or other acid. 1 c.c. of 10 % potassium cyanide solution is added, then a considerable excess of ammonia. If the solution is now colourless, it only remains to add a few drops of sodium sulphide

* *The Analyst*, 1908, **33**, 173.

† Report (No. 2) on Lead and Arsenic in Tartaric acid, Citric acid, and Cream of Tartar, 1907.

‡ *J. S. C. I.* 1909, **28**, 636, and 1910, 7.

solution and compare the colour produced with that developed by a solution containing a known amount of lead and treated precisely as detailed above. If the ammoniacal liquid is coloured, iron is present, and, if originally present in the ferrous state, it is only necessary to heat the solution to boiling, when the colour disappears, and on cooling to add the sulphide. When, however, ferric iron is present another portion of the substance must be dissolved, acidified, and a few drops of $^{N}/_{10}$ sodium thiosulphate added—the exact amount required depending on the amount of iron present. The solution is heated slowly to incipient boiling, allowed to stand until the colour suddenly disappears, and then potassium cyanide, etc., added as usual.

MAGNESIUM.

$Mg = 24{\cdot}32.$

An alkalimetric process for the determination of this substance has been adopted by Stolba, a reference to which is made under Phosphoric Acid, p. 114, but the time and trouble required to wash out the ammonia by alcohol renders the method too difficult for general purposes. A much shorter procedure has been devised by R. K. Meade.*

The method is based on the same principles as Williamson's process described under "Arsenic," p. 156. He found that when a solution of arsenic acid contained sufficient sulphuric or hydrochloric acid the arsenic is quickly reduced to arsenious acid even in the cold. For every molecule of arsenic acid so reduced there corresponds two atoms of magnesium, and two molecules or four atoms of iodine are liberated. This latter is titrated with sodium thiosulphate, and from the volume of standard solution required the magnesium is calculated.

The standard solutions are conveniently made as follows :—

Standard sodium arsenate is prepared by dissolving 12·29 gm. of pure arsenious acid in nitric acid, evaporating on a water-bath to dryness, neutralizing with sodium carbonate in solution, and when dissolved made up to a litre with distilled water. Each c.c. =0·005 gm. of Mg.

The standard solution of sodium thiosulphate is made to correspond to this either by direct titration, or by making it equal to a standard iodine solution made by dissolving 52·24 gm. of pure iodine, and 75 gm. of potassium iodide in about 200 c.c. of water, and making up to one litre. Each c.c. =0·005 gm. Mg.

Method of Procedure: Pour the magnesia solution, which should not contain too great an excess of ammonium chloride or oxalate, into a conical flask or a gas-bottle of sufficient size. Add one-third the volume of the solution of strong ammonia and 50 c.c. of sodium arsenate. Cork up tightly and shake vigorously for ten minutes. Allow the precipitate to settle somewhat, then filter and wash with a mixture of water and strong ammonia (3 : 1) until the washings cease to react for arsenic ; avoid, however, using an excess of the washing fluid. Dissolve the precipitate in dilute hydrochloric acid (1 : 1), allowing the acid solution to run into the flask in which the precipitation was made, and wash the filter-paper with the dilute acid, until the washings and solution measure 80 or 100 c.c. Cool, and add from 3 to 5 gm. of potassium iodide, free from iodate; allow the solution to stand for a few minutes, and then run in the standard thiosulphate until the colour of the liberated iodine fades to a pale straw colour. Add starch, and titrate until the blue colour of the iodide of starch is discharged.

* *J. Am. C. S.* **21**, 746.

If preferred, an excess of thiosulphate may be added, then starch and standard iodine until the blue colour is produced. On adding the iodide of potassium to the acid solution, a brown precipitate forms, which, however, dissolves when the thiosulphate is added.

Experience has proved that the whole process can be done within an hour, and the results in the case of dolomite, limestone, slag and cement are very near those given by gravimetric methods.

Frankforter and Cohen * state that a much sharper end-reaction is obtained if starch indicator is not used. They apply the process to *the determination of magnesium in water*, thus :—

500 c.c. of the water, after removal of iron and calcium as usual, are acidified, evaporated to 100 c.c., 33 c.c. of strong ammonia and 25 c.c. of a 10 % solution of sodium arsenate added, and the flask shaken vigorously for 10 minutes. The precipitate is filtered off, washed with the least possible amount of dilute ammonia, dissolved in 25 c.c. dilute sulphuric acid (1 : 4) into the original flask, the filter washed with 50 c.c. hot water, and 10 c.c. sulphuric acid (1 : 1) added. After cooling, 3—5 gm. of potassium iodide are added, the solution allowed to stand for 5 minutes, then the liberated iodine titrated with thiosulphate without starch indicator.

MANGANESE.

$Mn = 54{\cdot}93, \quad MnO = 70{\cdot}93, \quad MnO_2 = 86{\cdot}93.$

Factors.

$$\begin{aligned}
\text{Metallic iron} \times 0{\cdot}6350 &= MnO. \\
\text{,, \quad ,,} \times 0{\cdot}4918 &= Mn. \\
\text{,, \quad ,,} \times 0{\cdot}7783 &= MnO_2. \\
\text{Double iron salt} \times 0{\cdot}0907 &= MnO. \\
\text{Cryst. oxalic acid} \times 0{\cdot}6896 &= MnO_2. \\
\text{Double iron salt} \times 0{\cdot}1112 &= MnO_2.
\end{aligned}$$

1 c.c. $^N/_{10}$ solution $= 0{\cdot}003547$ gm. MnO or $= 0{\cdot}004347$ gm. MnO_2.

All the oxides of manganese, with the exception of the first or protoxide, when boiled with hydrochloric acid, yield chlorine in the following ratios :—

$$\begin{aligned}
Mn_2O_3 &= 1 \text{ eq. } O = 2 \text{ eq. Cl.} \\
Mn_3O_4 &= 1 \text{ eq. } O = 2 \text{ eq. Cl.} \\
Mn\ O_2 &= 1 \text{ eq. } O = 2 \text{ eq. Cl.} \\
Mn\ O_3 &= 2 \text{ eq. } O = 4 \text{ eq. Cl.} \\
Mn_2O_7 &= 5 \text{ eq. } O = 10 \text{ eq. Cl.}
\end{aligned}$$

The chlorine so produced can be allowed to react upon a known weight of ferrous salt ; and when the reaction is completed, the unchanged amount of iron salt is found by permanganate or dichromate.

Or, the chlorine may be led by a suitable arrangement into a solution of potassium iodide, there setting free an equivalent quantity of iodine, which is found by the aid of sodium thiosulphate.

Or, in the case of manganese ores, the reaction may take place with oxalic acid, resulting in the production of carbonic acid, which can be weighed as in Fresenius' and Wills' method, or

* *J. Am. Chem. Soc.* 1907, 1464

the amount of unchanged acid remaining after the action can be found by permanganate.

The largely increased use of manganese in the manufacture of steel has now rendered it imperative that some rapid and trustworthy methods of determination should be devised, and this has been done by well-known chemists. The first method described appears to have been simultaneously suggested by Pattinson and Kessler; both have succeeded in finding a method of separating manganese as dioxide of perfectly definite composition. Pattinson* found that the regular precipitation was secured by ferric chloride, and Kessler by zinc chloride. Wright and Menke have experimented on both processes with equally satisfactory results, but give a slight preference to zinc. Pattinson titrates the resulting MnO_2 with standard dichromate, and Kessler with permanganate.

1. Precipitation as MnO_2 and Titration with Dichromate (Pattinson).

The author's own description of the method is as follows :—

This method depends upon the whole of the manganese being precipitated as hydrated dioxide by calcium carbonate when chlorine or bromine is added to a solution of manganous salt containing also a persalt of iron or a salt of zinc, and under certain conditions of temperature, etc. This method is now adopted by many chemists both in private laboratories and in the laboratories of steel works ; and it is therefore thought that the following description of it in its slightly modified form, as now used for determining manganese in manganiferous iron ores, manganese ores, spiegeleisen, ferromanganese, etc., will not be out of place.

Method of Procedure : A quantity of the sample to be analysed, containing not more than about 0·25 gm. of manganese, is dissolved in hydrochloric acid. In the case of spiegeleisen and ferromanganese, about 3—4 c.c. of nitric acid are afterwards added to oxidize the iron. In the case of manganese ores, ferromanganese, and manganese slags, which do not contain as much iron as manganese, there is added to the solution as much iron, in the form of ferric chloride, as will make the quantities of iron and manganese in the solution about equal. An excess of iron is no drawback, except that a larger precipitate has afterwards to be filtered and washed.

The excess of acid in the solution is then neutralized by the addition of calcium carbonate, which is added until a slight reddening of the solution is produced. The solution is then rendered very slightly acid by dropping into it just enough hydrochloric acid to remove the red colour.

Then add in all cases 30 c.c. of a solution of zinc chloride containing 0·5 gm. of metallic zinc. The liquid is then brought to the boiling point, and diluted with boiling water to about 300 c.c.

60 c.c. of a solution of calcium hypochlorite, made by dissolving about 33 gm. of bleaching powder per litre and filtering, are then poured into the manganese solution ; but to the hypochlorite solution, before pouring it into the manganese solution, there should be added just enough hydrochloric acid to give it a faint permanent greenish-yellow colour after gentle agitation.

* *J. C. S.* 1879, 365, also *J. S. C. I.* **10**, 337.

The object of this addition of acid is to prevent a precipitate forming when the hypochlorite is added, due to the alkalinity of this solution. When hydrochloric acid is added in this way to the solution of calcium hypochlorite, the manganese solution remains clear on the addition of the calcium hypochlorite, and any possible local precipitation of manganese in a lower state of oxidation than MnO_2 is obviated.

Finally, add to the manganese solution about 3 gm. of calcium carbonate diffused in about 15 c.c. of boiling water. After the first evolution of carbonic acid has ceased, during which time the cover is kept on the beaker, the precipitate is stirred to make it collect together, and 2 c.c. of alcohol or methylated spirit are added and it is again stirred.

The precipitate is then thrown upon a large filter and washed, at first with cold water until the greater part of the chlorine is removed, and afterwards, to make the washing more rapid, with warm water at about 155° F. (65° C.). It is washed until, after draining, a drop shaken down straight from the precipitate by gently jolting the funnel, shows no indication of chlorine when tested with a strip of iodized starch-paper. As a matter of practice two or three washings are given after there has ceased to be any indication of chlorine.

By carrying out the process in the manner here described, the temperature of the liquid, immediately after the precipitation is complete, is about 170° F. (77° C.), and it is found that the best and most constant results are obtained when the temperature after precipitation is near this point.

70 c.c. of an acidified solution of ferrous sulphate, containing about 0·7 gm. of iron, and made by dissolving crystallized ferrous sulphate in a mixture of one part of monohydrated sulphuric acid and three parts of water, are then accurately measured off by a pipette and run into the beaker in which the precipitation was made. The filter paper, together with the precipitate, is then removed from the funnel and placed in the solution of ferrous sulphate in the beaker. The precipitate readily dissolves even in the cold (sometimes it may be necessary to add a little more acid to dissolve the ferric hydrate completely), the manganese dioxide converting its equivalent of ferrous sulphate into ferric sulphate. A sufficient quantity of cold water is now added, and the ferrous sulphate still remaining is titrated with a standard solution of potassium dichromate.

The exact amount of ferrous sulphate in 70 c.c. of the ferrous sulphate solution is determined by measuring off into a clean beaker another portion of 70 c.c. and titrating with standard dichromate solution. The difference between the amounts of that solution required gives the quantity of ferrous sulphate oxidized by the manganese dioxide, and from this the percentage of manganese in the sample can be calculated.

The ferrous sulphate solution should be standardized from day to day, as it undergoes slow oxidation on exposure to air.

A solution of bromine in water may of course be used instead of the hypochlorite solution, in which case no acid is added to the bromine solution. When using bromine, a solution containing about 0·7 gm. of bromine (about 22 gm. per litre) should be used, and 90 c.c. of this solution used for precipitating about 0·25 gm. of manganese.

The unpleasantness of working with bromine may be mitigated, to some extent, by adding to the bromine solution, before pouring it into the liquid containing the manganese, a few drops of a solution of sodium hydrate until nearly all, but not quite all, the bromine is taken up. If an excess of sodium hydrate were added to the bromine it would produce a precipitate on pouring it into the manganese solution, and this is to be avoided.

It is preferable to have both zinc and iron in solution with the manganese. When working with either of these alone all the manganese is obtained in the form of dioxide, but with iron alone there is a greater tendency to the formation of permanganate than when zinc is also present. This point was also noticed by Wright and Menke.* When zinc alone is present, it is found that the precipitation of the dioxide does not take place so rapidly as when iron is also present. When both iron and zinc are used, there is very seldom any permanganate formed, if

* *J. C. S. Trans.* 1883, 43.

care is taken not to use an unnecessarily large excess of chlorine or bromine, but occasionally there is a small quantity formed, especially if the precipitate is left to stand some considerable time before filtering. It was found that the addition of a very small quantity of alcohol immediately after the precipitation of the manganese is complete entirely prevents the formation of permanganate even when a large excess of chlorine has been used, and for this reason it is well to add it.

When filtering paper has been wetted with the solution containing free chlorine or bromine and afterwards washed clean, it has no reducing action either upon potassium dichromate or upon ferric sulphate. The addition of the filter together with the precipitate to the solution of ferrous sulphate, therefore, does not influence the result.

It must be pointed out that the presence of lead, copper, nickel, cobalt, and chromium in the substances under examination interferes with the accuracy of this method of titrating manganese.

It was found that so large a proportion as 1 per cent. of lead, copper, and nickel does not greatly interfere with the test, but the interference of cobalt, and especially of chromium, is serious. All these substances, except chromium, form, under the conditions of the test, higher oxides insoluble in water, which are precipitated with the manganese dioxide, and which oxidize ferrous sulphate to ferric sulphate; whilst chromium forms some insoluble chromate which goes down with the manganese dioxide.

Fortunately these metals rarely, if ever, occur in the ores of manganese or in spiegeleisen and ferromanganese in sufficient quantity to affect the practical accuracy of this test.

This volumetric method cannot, however, be applied to the determination of manganese in alloys of these metals, such as ferrochrome or in ores containing these metals, without previously separating them from the solution containing the manganese.

$$1 \text{ c.c. } {}^{N}/_{10} \text{ dichromate} = 0{\cdot}002747 \text{ gm. Mn.}$$

The above is undoubtedly one of the best volumetric methods known for the determination of manganese in various compounds and ores; but Saniter* in criticising the method gives it the credit for yielding slightly low results, and advocates the standardizing of the dichromate, not upon iron, but upon a manganese oxide of known composition.

Atkinson† gives the following short description of the method as practically in daily use in a large steel works.

Weigh out 0·5 gm. or 0·6 gm. of an ore containing about 20 per cent. manganese, dissolve in 7 or 8 c.c. of strong HCl, and when dissolved, wash the whole, without filtering, into a large narrow-sided beaker. When cold it is neutralized with precipitated calcium carbonate, until the liquid assumes a reddish hue. 40 or 50 c.c. of saturated bromine water are added, and the mixture allowed to stand in the cold for half-an-hour. At the expiration of that time the beaker is nearly filled up with boiling water, and precipitated calcium carbonate added until there is no further effervescence, and part of the carbonate is evidently unacted upon. A small quantity of alcohol is then added, the whole well stirred, and the precipitate allowed to settle. The clear liquid is filtered off and fresh boiling water added to the residue in the beaker, a little alcohol being used to reduce any permanganate which is formed. The filtration and washing are repeated until the filtrate when cooled no longer turns iodized starch-paper blue. During the washing about 1·9 to 2·5 gm. of pure granular ferrous-ammonium sulphate are weighed out, washed into the beaker in which the precipitation took place, and about 30 to 50 c.c. of dilute sulphuric acid added. The filter containing the precipitated MnO_2, is then placed in the beaker, and

* *J. S. C. I.* **13**, 112. † *J. S. C. I.* **5**, 365.

the latter is quickly dissolved by the oxidation of a portion of the ferrous salt into ferric sulphate. The remaining ferrous iron is then titrated with dichromate in the usual way. The difference between the number of c.c. of dichromate used and the number which the original weight of the ferrous-ammonium sulphate would have required if directly titrated is a measure of the quantity of MnO_2 present. For rapidity and simplicity this volumetric process leaves nothing to be desired; duplicate experiments agree within very narrow limits; and if the assumption be accepted that the presence of ferric chloride effects the complete oxidation of the manganese to the state of peroxide, no other process can compete with it.

Pattinson prefers to use bleach solution to bromine, because the formation of permanganate is more easily seen. In any case not more than a trace of permanganate should be formed, and if the first experiment shows this to be the case, another trial must be commenced with less oxidizing material.

J. W. Westmoreland describes a modified method which is designed to overcome some objections raised against the above processes.

With ferro-manganese and ores containing about 50 to 60 % of Mn, about 0·4 gm. is taken; ores with 40 %, 0·5 gm.; manganiferous iron ores, with say about 20 % each of Fe and Mn, 0·75 gm.; spiegeleisen and silicospiegels, with about 25 % Mn, the same.

The material, having been brought into solution by any of the methods described, is concentrated to a small bulk in a large conical beaker. A solution of ferric chloride, containing about the same amount of iron as there is approximately of Mn, is added, together with a solution of zinc chloride, containing about 0·5 gm. of Zn. The excess of acid is then neutralized with caustic potash, so that the bulk of liquid is about 80 c.c. To this is added about 60 c.c. of saturated bromine water (more for ferro-manganese, less for manganiferous iron ores) and zinc oxide emulsion* is gradually dropped in with shaking, until the Fe and Mn are precipitated, (care must be taken to avoid a large excess of zinc oxide). The beaker is then filled up with boiling tap-water, and the clear liquid poured through a filter, previously adding a few drops of alcohol. The beaker is then filled with boiling water five times in succession, the precipitate being stirred up with the hot water each time of washing and allowed to settle. It is then brought on the filter, and again freely washed with boiling distilled water. The filter and contents are then transferred to the beaker, an excess of acid solution of ferrous sulphate added, and when the precipitate is dissolved the liquid is diluted with cold distilled water, and the excess of ferrous iron determined at once with permanganate. The value of the iron solution in metallic iron is found by titrating the same volume of iron solution as has actually been used for dissolving the Mn precipitate, and the Fe oxidized multiplied by 0·4918 = Mn.

It is absolutely necessary, in order to get accurate results, to wash the precipitate as thoroughly as mentioned.

$$2KMnO_4 + 3MnO = K_2O + 5MnO_2$$

$$1 \text{ c.c. } {}^{N}/_{10} \text{ permanganate} = \cdot 001648 \text{ gm. Mn.}$$

* The emulsion of zinc oxide may, of course, be readily made by rubbing down pure zinc oxide in water so as to be of about the consistence of cream. Emmerton (*Trans. Amer. Inst. Min. Eng.* **10**, 201), suggests the following method of preparing this reagent. Dissolve ordinary zinc white in HCl, add the powder until there remains some undissolved, then add a little bromine water; heat the mixture, filter and precipitate the zinc oxide from the filtrate with the slightest possible excess of ammonia. Wash thoroughly by decantation, and finally wash into a bottle with approximately enough water to give a proper consistence. By this method a very finely divided oxide is obtained, owing to its not being dried.

2. Volhard's Permanganate Method.

This is now largely used by Continental and American chemists, especially with certain modifications*; the details of the original process being as follows :—

A quantity of material is taken so as to contain from 0·3 to 0·5 gm. Mn, dissolved in hydrochloric or nitric acid, evaporated in porcelain to dryness, first adding a little ammonium nitrate, then heated over the flame to destroy organic matter. The residue is digested with HCl, a little strong H_2SO_4 added, and again evaporated to dryness, first on the water-bath, then with greater heat till vapours of SO_3 are evolved. It is then washed into a litre flask and neutralized with sodium hydrate or carbonate ; sufficient pure zinc oxide, made into a cream, is added to precipitate all the iron. The flask is filled to the mark, shaken, and 200 c.c. filtered off into a boiling flask, acidified with 2 drops of nitric acid, (sp. gr. 1·2), heated to boiling, and titrated with $^N/_{10}$ permanganate while still hot. Owing to the presence of the trace of nitric acid, most operators now deduct 0·2 c.c. of permanganate before calculating the manganese.

Särnström's method of using this process for determining manganese in iron ores, as described by Mixer and Du Bois, is to precipitate the iron in hot dilute solution by sodium carbonate, care being taken to add no more than is just sufficient to precipitate the iron ; then titrating (without filtering off the ferric oxide) with permanganate. Using the soda in this way does not give perfect neutralization, yet it gives excellent results, as shown by both Mixer and Du Bois and G. Auchy. This is difficult to explain, as mentioned by the latter chemist, because in working either Volhard's method or Stone's modification of it, there must be a much larger quantity of zinc emulsion used than is necessary to precipitate the iron, in order to avoid too high results. But all experiments show that Särnström's process is quite free from this error. Auchy is of opinion that either the ferric oxide, by its presence, in some way prevents high results being obtained when solutions are incompletely neutralized, or by its presence prevents the precipitation of manganese dioxide, unless the solution be thoroughly neutralized when titrated ; the permanganate simply colouring the solution, and no manganese being precipitated unless more sodium carbonate is added.

G. E. Stone's modification of the original Volhard's method gives an easier and quicker result, as no evaporation with sulphuric acid is needed, and the precipitate of ferric oxide rapidly subsides in the faintly acid nitric acid solution.

Method of Procedure : The necessary precautions, as given by G. Auchy, are printed in italics. 3·3 gm. of drillings are dissolved in 50 c.c. of nitric acid (sp. gr. 1·20) and washed into a 500 c.c. measuring flask. Two-thirds of the amount of sodium carbonate solution necessary for complete neutralization are added, and the *liquid cooled.* Zinc oxide emulsion is then added until the solution stiffens, an *excess being avoided.* After dilution to about three-fourths the capacity of the flask the whole is allowed to stand until the ferric oxide begins to settle,

* Modifications of Volhard's original method have been discussed by
Mayer, *Z. angew. Chem.* 1907, 1980, and *Analyst* 1908, 34 ;
Heike, *Stahl u. Eisen*, 1909, 1921, and *J. S. C. I.* 1910, 114 ;
Deiss, *Chem. Zeit.* 1910, 237, and *J. S. C. I.* 1910, 456.
Fischer, *Z. anal. Chem.* 1909, 751, and *J. S. C. I.* 1910, 47.

and a *considerable excess of zinc oxide emulsion then added* to the colourless solution. After being made up to the mark and well shaken, the precipitate is allowed to settle, and 250 c.c. of the clear solution heated in a flask to boiling and titrated with permanganate of strength 0·0056. After making the necessary deductions for impurities in the sodium carbonate and zinc oxide (which have been previously ascertained), the number of c.c. of permanganate taken is divided by 10, and 0·02 *per cent. deducted* from the result.

Fischer's Modification of Volhard's Method.* This modification is claimed to give accurate results in the presence of chlorides and when titrating with a solution of permanganate standardized by oxalic acid, without the use of a correcting factor. A solution of manganous salt, containing hydrochloric or sulphuric acid, is treated as follows:—

Sodium hydroxide is added until a slight precipitate appears; this is redissolved with a few drops of sulphuric acid, 1 gm. of freshly ignited zinc oxide and 10 gm. of zinc sulphate are added, and the solution is titrated with permanganate, with frequent boiling and shaking. *Then 1 c.c. of pure glacial acetic acid is added* and the liquid is boiled; this discharges the pink colour, apparently owing to the liberation of absorbed manganous salt from the precipitate, which becomes flocculent and settles, and the liquid is again titrated until the pink colour is restored, the total volume of permanganate used being taken as that required to react with the manganese. If sulphates only be present, about 10 gm. of zinc sulphate are added for every 10 c.c. of $^{N}/_{10}$ permangate used. Iron when present, as in the analysis of ferromanganese, is, as usual, precipitated with zinc oxide, and manganese is determined in the filtrate.

Cahen and Little† have investigated this modification and find that it gives very consistent results.

3. Determination by conversion into Permanganic Acid.

This method, in which the manganese is oxidized to permanganic acid by bismuth peroxide in the presence of nitric acid, was originally devised by Schneider. Further experiments were afterwards carried on by Reddrop and Ramage‡, the result of which was that they used sodium bismuthate in the solid state for the conversion of the manganese.

Their paper gives details of the experiments on ferro-manganese, spiegel, silico-spiegel, iron and steel, too voluminous to be reproduced here; but the final method for wronght iron, steel, and pig iron is as follows:—

Weigh out 1·1 gm. of the sample, and place it in a beaker or boiling-tube; add 30 c.c. of dilute nitric acid (sp. gr. 1·2) and boil. If a part remains undissolved, decant the solution, filter off carbonaceous matter if necessary, and add more nitric acid up to 25 c.c. If the sample dissolves completely, use the 25 c.c. of acid to wash the tube. If the sample contains much silicon, care must be taken, when boiling, not to concentrate the acid unduly, or the silicic acid will separate in a form which blocks up the filter.

Cool the solution in a beaker to about 16°, oxidize with 2 gm. of sodium bismuthate, stir for three minutes, and filter through an asbestos filter into a clean flask. Add $^{N}/_{10}$ hydrogen peroxide solution from a burette until the

* *Z. a. Chem.* 1909, **48**, 751–760. † *Analyst*, 1911. ‡ *J. C. S.* **66**, 268.

reddish colour disappears; then add from 1·5 to 3·0 c.c. in excess, and titrate with $^{N}/_{10}$ potassium permanganate.

Each c.c. of $^{N}/_{10}$ hydrogen peroxide reduced by the sample = 0·1 per cent. of manganese.

The reddish colour mentioned above is produced by a secondary reaction during the titration, probably between the permanganic acid and the reduced manganous nitrate. A small quantity of manganic salt appears to be formed, and the yellow colour of this masks the colour of the permagnanic acid. This yellow solution is more difficult to reduce than the solution of permanganic acid, and the tinctorial power of the compound is much less than that of the acid; hence the necessity for adding an excess of hydrogen peroxide.

Hydrochloric acid must be absent. The results are within 0·01 per cent. of the manganese present.

A modification of this method has been adopted by Ibbotson and Brearley.*

These authors consider that the reduction of the permanganate during and after filtration is caused by the presence of carbon. It is, therefore, essential to complete the oxidation of the carbon in hot solution, and this should certainly be done with high carbon steels. The method generally adopted by them is as follows:—

Dissolve 1·1 gm. of the metal in 35 c.c. of 1·20 nitric acid, and then add sodium bismuthate a little at a time to the somewhat cooled solution until a permanganate colour persists, or on boiling is decomposed to manganic oxide. Clear up the permanganate or the dioxide precipitate with a little hydrogen peroxide, sulphurous acid, or ferrous sulphate free from manganese. Cool the solution, and add about 10 c.c. of water and a considerable excess of bismuthate. Filter, wash with dilute (3 or 4 per cent.) nitric acid, and titrate with $^{N}/_{10}$ permanganate.

Unlike hydrogen peroxide, the excess of ferrous sulphate does not react with ferric nitrate, and is therefore preferable. It can be safely used in cold nitric acid solutions as above, if the titration is not needlessly delayed. Molybdenum, titanium, and vanadium do not interfere in this modification as they do in Reddrop and Ramage's process. If chromium be present, it is liable to be slowly but completely oxidized by bismuthate to chromic acid, thus giving high results for manganese. The bismuthate should therefore be added, and the solution shaken and filtered quickly. The presence of tungsten introduces no error; but in steels containing much tungsten, and particularly in chrome tungsten steels, the precipitate has a tendency to pass through the filter. As the joint presence of tungsten and hydrofluoric acid causes the results to be high and very erratic, the hydrofluoric acid should be previously driven off with sulphuric acid.

For the application of this process to steels, ores, etc., see A. A. Blair, *J. Am. Chem. Soc.*, **26**, 793.

A simplification of Reddrop and Ramage's process has been made by Dufty† for use in iron works.

This colorimetric process is as follows:—The nitric acid solution is transferred (after the carbon has been determined by the Eggertz method) to a graduated stoppered test-mixer, the carbon tube being rinsed out into the mixer, and the solution then made up to a definite volume with nitric acid (sp. gr. 1·20, is used throughout). A standard steel, of known Mn content, is treated in like manner, being diluted to the same volume as the sample. Equal quantities of bismuthate are then added through a dry funnel, and the contents thoroughly mixed, the mixing being repeated five minutes later. After being allowed to settle in a dark cupboard, which usually takes about thirty minutes, measured quantities

* *C. N.* **84**, 247. † *C. N.* **84**, 248.

of the clear pink solutions are transferred by means of a pipette to stoppered carbon tubes, and the colours compared in the usual manner.

In practice it has been found most convenient to weigh out 0·1 gm. of steel, dissolving in 2 or 3 c.c. HNO_3, according to carbon content, and after the carbon has been determined transferring to 25 c.c. test-mixers, and diluting with HNO_3 to 20 c.c. if the manganese be under 0·8 per cent., or to 25 c.c. if over that percentage. 0·2 gm. bismuthate is then added to each tube, and after mixing and allowing to settle exactly 5 c.c. are transferred to the comparing tubes, the standard being diluted to a convenient tint for comparison (e.g., 0·82 standard to 16·4 c.c.). The standard used for the carbon determination may conveniently be used for determining the manganese, and one standard solution will serve for a batch of determinations as in the carbon colorimetric test.

The above modification of the "bismuthate process" has been used for some time with satisfaction. For steel works with Siemens or Bessemer plant, where a large number of analyses have to be made as rapidly as possible, the advantages of this modification over the original volumetric process are obvious; a considerable saving in time not only being effected, but 90 per cent. less "bismuthate" is required for each determination.

Metzger and McCrackan* Modification of the Bismuthate Method.—This depends on the fact that, in hot sulphuric acid solution, sodium bismuthate oxidizes manganese to the quadrivalent condition (not to permanganate), and to the further fact that in cold sulphuric acid solution the oxidizing power of sodium bismuthate is so restricted, that it is unnecessary to remove the excess of bismuthate from the cooled solution by filtration before proceeding to the titration of the quadrivalent manganese.

Method of Procedure: To the manganese solution 10 to 15 c.c. of sulphuric acid are added, together with sufficient water to bring the volume up to 60 or 70 c.c. The mixture is allowed to cool, and then 1 to 2 gm. of sodium bismuthate are introduced into the flask in such a way that none sticks to the neck or sides. The flask is placed in a cold water-bath, which is then heated to boiling, and kept boiling for twenty minutes. The contents of the flask are cooled under the tap, a measured amount of standard ferrous sulphate solution, more than sufficient to react with the tetravalent manganese, is added, the solution diluted to 200 c.c., and the excess of ferrous sulphate determined by titration with permanganate. Mn = 2Fe. The extreme error of the method is 0·3 c.c. of $^{N}/_{10}$ solution, and manganese is never over-estimated.

4. Persulphate Method (Knorre).†

In this method the manganese is oxidized by means of ammonium persulphate and precipitated as hydrated manganese dioxide, which is filtered off, treated with hydrogen peroxide or ferrous sulphate, and titrated with permanganate, as in the previous method.

Method of Procedure: The solution containing manganese (such a quantity as will contain about 0·1 gm. of the metal) is placed in a capacious Erlenmeyer flask, and ammonium persulphate added (50—100 c.c. of a solution containing about 60 gm. per litre). The liquid is boiled for about five minutes, and the precipitated manganese dioxide filtered and washed. It is then transferred (with the filter) to the flask in which it was precipitated, dilute sulphuric acid is added, followed by a known quantity of a titrated dilute solution of hydrogen

* *J. Amer. Chem. Soc.*, 1910, **32**, 1250. † *Z. angew. Chem.*, 1901, 1149.

peroxide. After the precipitate is completely dissolved, the excess of hydrogen peroxide is determined by standard potassium permanganate, and the manganese is calculated from the amount of permanganate equivalent to the hydrogen peroxide destroyed. Instead of hydrogen peroxide, ferrous sulphate may be used.

The author standardizes his permanganate solution by carrying the method through on a known quantity of manganese ammonium sulphate, potassium permanganate, or other manganese compound of definite composition. When the permanganate is standardized by iron or ferrous salts, the method gives results about $1\frac{1}{2}$ per cent. too low, though gravimetric determinations indicate that the manganese is completely precipitated by the boiling with persulphate.

Schmidt* oxidizes the manganese by persulphate in the presence of silver nitrate, and makes the determination colorimetrically.

5. Technical Examination of Manganese Ores used for Bleaching Purposes, etc.

The ore, when powdered and dried for analysis, rapidly absorbs moisture on exposing it to the air, and consequently has to be weighed quickly ; it is better to keep the powdered and dried sample in a small light stoppered bottle, the weight of which, with its contents and stopper, is accurately known About 1 or 2 gm. or any other quantity within a trifle, can be emptied into the proper vessel for analysis, and the exact quantity found by reweighing the bottle.

A hardened steel or agate mortar must be used to reduce the mineral to the finest possible powder, so as to ensure its complete and rapid decomposition by the hydrochloric acid.

Considerable discussion has taken place as to the best processes for determining the available oxygen in manganese ores, arising from the fact that many of the ores now on the market contain iron in the ferrous state ; and if such ores be analysed by the usual iron method with hydrochloric acid, a portion of the chlorine produced is employed in oxidizing the iron contained in the original ore. Such ores, if examined by Fresenius' and Wills' method, show therefore a higher percentage than by the iron method, since no such consumption of chlorine occurs in the former process. Manufacturers have therefore refused to accept certificates of analysis of such ores when based on Fresenius' and Wills' method. This renders the volumetric processes of more importance, and hence various experiments have been made to ascertain their possible sources of error.

The results show that the three following methods give very satisfactory results.†

6. Direct Analysis by Distillation with Hydrochloric Acid.

This is the quickest and most accurate method of finding the quantity of available oxygen present in any of the ores of manganese

* *J. Amer. Chem. Soc.*, **32**, 965, and *Analyst*, 1910, 454.

† See Scherer and Rumpf, *C. N.* **20**, 302 ; also Pattinson, *ibid.* **21**, 266 ; and Paul, **21**, 16.

or mixtures of them. It also possesses the recommendation that the quantity of chlorine which they liberate is directly expressed in the analysis itself; and, further, gives an estimate of the quantity of hydrochloric acid required for the decomposition of any particular sample of ore, which is a matter of some moment to the manufacturer of bleaching powder.

The apparatus for the operation may be those shown in figs. 38 or 39. For precautions in conducting the distillation see p. 135 et seq.

METHOD OF PROCEDURE: In order that the percentage of dioxide shall be directly expressed by the number of c.c. of $^{N}/_{10}$ thiosulphate solution used, 0·4347 gm. of the properly dried and powdered sample is weighed and put into the little flask; solution of potassium iodide in sufficient quantity to absorb all the iodine set free is put into the large tube (if the solution containing $\frac{2}{10}$ eq. or 33·2 gm. in the litre be used, about 70 or 80 c.c. will in ordinary cases be sufficient); very strong hydrochloric acid is then poured into the distilling flask, and the operation conducted as on p. 137. Each equivalent of iodine liberated represents 1 eq. Cl, also 1 eq. MnO_2.

Instead of using a definite weight, it is well to do as before proposed, namely, to pour about the quantity required out of the weighed sample-bottle into the flask, and find the exact weight afterwards.

Barlow* records a good method of separating Mn from the metals of its own group as well as from alkalies and alkaline earths.

For the quantitative determination of Fe and Mn in the same solution as chlorides (other metals except Cr and Al may be present, but are best absent), solution of NH_4Cl is first added, then strong NH_4HO in excess, boil, then add hydrogen peroxide so long as a precipitate falls, boil for a few minutes, filter, wash with hot water, ignite, and weigh the mixed oxides together as $Fe_2O_3+Mn_3O_4$.

The oxides are then distilled with HCl, and the amount of iodine found by thiosulphate.

The weight of mixed oxides, minus the Mn_3O_4, gives the weight of Fe_2O_3.

Pickering† has pointed out that pure manganese oxides, freshly prepared, or the dry oxides in very fine powder, may be rapidly determined without distillation by merely adding them to a large excess of potassium iodide solution in a beaker, running in 2 or 3 c.c. of hydrochloric acid, when the oxides are immediately attacked and decomposed; the liberated iodine is then at once titrated with thiosulphate. Impure oxides, containing especially ferric oxide, cannot however be determined in this way, since the iron would have the same effect as manganic oxide; hence distillation must be resorted to in the case of all such ores, and it is imperative that the strongest hydrochloric acid should be used.

Pickering's modified process is well adapted to the examination of the Weldon mud for its available amount of manganese dioxide.

* *C. N.* **53**, 41. † *J. C. S.* 1880, 128.

7. Determination by Oxalic Acid.

The very finely powdered ore is mixed with a known volume of normal oxalic acid solution, sulphuric acid added, and the mixture heated and well shaken, to bring the materials into intimate contact and liberate the CO_2. When the whole of the ore is decomposed, which may be known by the absence of brown or black sediment, the contents of the vessel are made up to a definite volume (say 300 c.c.), and 100 c.c. of the dirty milky fluid well acidified, diluted, and titrated for the excess of oxalic acid by permanganate. If, in consequence of the impurities of the ore, the mixture be brown or reddish coloured, this would of course interfere with the indication of the permanganate, and consequently the mixture in this case must be filtered; the 300 c.c. are, therefore, well shaken and poured upon a large filter. When about 100 c.c. have passed through, that quantity can be taken by the pipette and titrated as in the former case.

If the solution be not dilute and freely acid, it will be found that the permanganate produces a dirty brown colour instead of its well-known bright rose-red ; if the first few drops of permanganate produce the proper colour immediately they are added, the solution is sufficiently acid and dilute.

If 4·347 gm. of the ore be weighed for analysis, the number of c.c. of normal oxalic acid will give the percentage of dioxide ; but as that is rather a large quantity, and takes some time to dissolve and decompose, half the quantity may be taken, when the percentage is obtained by doubling the volume of oxalic acid used.

This process possesses an advantage over the following, inasmuch as there is no fear of false results occurring from the presence of air. The analysis may be broken off at any stage, and resumed at the operator's convenience.

8. Determination by Iron.

Iron wire of 99·8 % purity can readily be obtained ; but if a perfectly dry and unoxidized double iron salt be at hand, its use saves time. 1 mol. of this salt(=392·17), representing 43·47 of MnO_2, consequently, 1 gm. of the latter requires 9·022 gm. of the double salt; or in order that the percentage shall be obtained without calculation 1·108 gm. of ore may be weighed and digested in the presence of free sulphuric acid, with 10 gm. of double iron salt, the whole of which would be required supposing the sample were pure dioxide. The undecomposed iron salt remaining at the end of the reaction is determined by permanganate or dichromate ; the quantity so found is deducted from the original 10 gm., and if the remainder be multiplied by 10 the percentage of dioxide is arrived at.

Instead of this plan, which necessitates exact weighing, any convenient quantity may be taken from the tared bottle, as before described, and digested with an excess of double salt, the weight of which is known. After the undecomposed quantity is found by

permanganate or dichromate, the remainder is multiplied by the factor 0·111 (or $\frac{1}{9}$), which gives the proportion of dioxide present, whence the percentage may be calculated.

The decomposition of the ore may be made in any of the apparatus used for titrating ferrous iron. The ore is first put into the decomposing flask, then the iron salt and water, so as to dissolve the salt to some extent before the sulphuric acid is added. Sulphuric acid should be used in considerable excess, and the flask heated till all the ore is decomposed; the solution is then cooled, diluted, and the whole or part titrated with permanganate or dichromate.

In the case of using $^N/_{10}$ dichromate for the titration, the following plan is convenient:—100 c.c. of $^N/_{10}$ dichromate = 3·922 gm. of double iron salt (supposing it to be perfectly pure), therefore if 0·4347 gm. of the sample of ore be boiled with 3·922 gm. of the double salt and excess of acid, the number of c.c. of dichromate required deducted from 100 will give the number corresponding to the percentage.

MERCURY.

$Hg = 200.$

1 c.c. $^N/_{10}$ solution = 0·0200 gm. Hg.
= 0·0208 gm. Hg_2O.
= 0·0271 gm. $HgCl_2$

Double iron salt × 0·5104 = Hg.
,, ,, × 0·6914 = $HgCl_2$.

1. Precipitation as Mercurous Chloride.

THE solution to be titrated must not be warmed, and must contain the metal in the form of protosalt only. $^N/_{10}$ sodium chloride is added in slight excess, filtered, and the precipitate washed with the least possible quantity of water to ensure the removal of all the sodium chloride; to the filtrate a few drops of chromate indicator are added, then pure sodium carbonate till the liquid is of a clear yellow colour, $^N/_{10}$ silver is then delivered in till the red colour appears. The quantity of sodium chloride so found is deducted from that originally used, and the difference calculated in the usual way.

2. By Ferrous Oxide and Permanganate (Mohr).

This process is based on the fact that when mercuric chloride (corrosive sublimate) is brought in contact with an alkaline solution of ferrous oxide in excess, the latter is converted into ferric oxide, while the mercuric is reduced to mercurous chloride (calomel). The excess of ferrous oxide is then found by permanganate or dichromate—

$$2HgCl_2 + 2FeCl_2 = Hg_2Cl_2 + Fe_2Cl_6.$$

It is therefore advisable in all cases to convert the mercury to be

determined into the form of sublimate, by evaporating it to dryness with nitro-hydrochloric acid; this must take place, however, below boiling heat, as vapours of chloride escape with steam at 100° C. (Fresenius).

Nitric acid or free chlorine must be altogether absent during the decomposition with the iron protosalt, otherwise the residual titration will be inexact, and the quantity of the iron salt must be more than sufficient to absorb half the chlorine in the sublimate.

EXAMPLE.—1 gm. of pure $HgCl_2$ was dissolved in warm water, and 3 gm. of double iron salt added, then solution of caustic soda till strongly alkaline. The mixture became muddy and dark in colour, and was well shaken for a few minutes, then sodium chloride and sulphuric acid added, continuing the shaking till the colour disappeared and the precipitate of ferric oxide dissolved, leaving the calomel white; it was then diluted to 300 c.c., filtered through a dry filter, and 100 c.c. titrated with $^N/_{10}$ permanganate, of which 13·2 were required—$13{\cdot}2 \times 3 = 39{\cdot}6$, which deducted from 76·5 c.c. (the quantity required for 3 gm. double iron salt), left 36·9 c.c. = 1·447 gm. of undecomposed iron salt, which multiplied by the factor 0·6914, gave 1·0005 gm. of sublimate, instead of 1 gm., or the 36·9 c.c. may be multiplied by the $^N/_{10}$ factor for mercuric chloride, which will give 1 gm. exactly.

3. By Iodine and Thiosulphate (Hempel).

If the mercury exist as a protosalt it is precipitated by sodium chloride, the precipitate well washed and together with its filter pushed through the funnel into a stoppered flask, a sufficient quantity of potassium iodide added, together with $^N/_{10}$ iodine solution (to 1 gm. of calomel about 2·5 gm. of iodide, and 100 c.c. of $^N/_{10}$ iodine), the flask closed, and shaken till the precipitate has dissolved—

$$Hg_2Cl_2 + 6KI + I_2 = 2HgK_2I_4 + 2KCl.$$

The brown solution is then titrated with $^N/_{10}$ thiosulphate till colourless, diluted to a definite volume, and a measured portion titrated with $^N/_{10}$ iodine and starch for the excess of thiosulphate. 1 c.c. $^N/_{10}$ iodine = 0·02 gm. Hg.

Where the mercurial solution contains nitric acid, or the metal exists as peroxide, it may be converted into protochloride by the reducing action of ferrous sulphate, as in Mohr's method. The solution must contain hydrochloric acid or common salt in sufficient quantity to transform all the mercury into calomel. Ferrous sulphate in solution in quantity equal to at least three times the weight of mercury present is to be added, then caustic soda in excess, the muddy liquid well shaken for a few minutes, then dilute sulphuric acid added in excess, and the mixture stirred till the dark-coloured precipitate has become perfectly white. The calomel so obtained is collected on a filter, well washed, and titrated with $^N/_{10}$ iodine and thiosulphate as above.

C. Reichardt* has recommended the following method of determining mercury A weighed quantity of the mercury compound is dissolved and converted into mercury arsenate by boiling with standard arsenious acid and caustic soda in excess. Metallic mercury is precipitated as a black powder. This is filtered and washed, and the amount of unoxidized arsenious acid in the filtrate is found by titration with standard iodine in the usual way.

* *Z. a. C.* 1898, 749.

4. As Mercuric Iodide (Personne).*

This process is founded on the fact that if a solution of mercuric chloride be added to one of potassium iodide, in the proportion of 1 equivalent of the former to 4 of the latter, red mercuric iodide is formed, which dissolves to a colourless solution until the balance is overstepped, when the brilliant red colour of the iodide appears as a precipitate, which, even in the smallest quantity, communicates its tint to the liquid. The mercuric solution must always be added to the iodide; a reversal of the process, though giving eventually the same quantitative reaction, is nevertheless much less speedy and trustworthy. The mercurial compounds to be determined by this process must invariably be brought into the form of neutral mercuric chloride.

The standard solutions required are decinormal, made as follows :—

Solution of potassium iodide.—33·2 gm. of pure salt to 1 litre. 1 c.c. = 0·01 gm. Hg. or 0·01355 gm. $HgCl_2$.

Solution of mercuric chloride.—13·546 gm. of the salt, with about 30 gm. of pure sodium chloride (to assist solution), are dissolved to 1 litre. 1 c.c. = 0·01 gm. Hg.

METHOD OF PROCEDURE: The conversion of various forms of mercury into mercuric chloride is, according to Personne, best effected by heating with caustic soda or potash, and passing chlorine gas into the mixture, which is afterwards boiled to expel excess of chlorine (the mercuric chloride is not volatile at boiling temperature when associated with alkali chloride). The solution is then cooled and diluted to a given volume, placed in a burette, and delivered into a measured volume of the decinormal iodide until the characteristic colour appears. It is preferable to dilute the mercuric solution considerably, and make up to a given measure, say 300 or 500 c.c.; and as a preliminary trial take 20 c.c. or so of iodide solution, and titrate it with the mercuric solution approximately with a graduated pipette; the exact strength may then be found by using a burette of sufficient size.

Iodimetric Method (Rupp)†. This can be used for mercuric nitrate, chloride, or sulphate, as well as for mercuric cyanide.

METHOD OF PROCEDURE: The solution of the mercury salt, containing about 0·2 gram of mercury in 25 to 50 c.c., is treated with excess of potassium iodide (1 gram) so that the mercuric iodide that forms is redissolved. The liquid is next rendered alkaline with sodium hydroxide, treated with 2 or 3 c.c. of 40 per cent. formaldehyde solution, diluted with 10 c.c. of water, and vigorously and continuously shaken for one to two minutes. It is then acidified with acetic acid, 25 c.c. of $^{N}/_{10}$ iodine solution added, and the excess of free iodine titrated with $^{N}/_{10}$ sodium thiosulphate solution. The formaldehyde precipitates the mercury, which combines with the iodine to form mercuric iodide, and the excess of iodine is titrated as described. If the mercury be in the form of mercurous salts, it must be brought into the mercuric state before precipitation, by treatment with Br. water, excess of Br. being removed by gentle heating. In the case of mercuric cyanide, sulphuric acid should be used instead of acetic acid for the acidification, so as to decompose any cyanogen iodide that may have been formed.

* *Compt. Rend.* **56**, 63. † *Ber.* 1906, **39**, 3702.

5. By Potassium Cyanide (Hannay).

This process is exceedingly valuable for the determination of almost all the salts of mercury when they occur, or can be separated, in a tolerably pure state. Organic compounds are of no consequence unless they affect the colour of the solution.

The method depends on the fact that free ammonia produces a precipitate or (when the quantity of mercury is very small) an opalescence in mercurial solutions, which is removed by a definite amount of potassium cyanide.

The delicacy of the reaction is interfered with by excessive quantities of ammoniacal salts, or by caustic soda or potash; but this difficulty is lessened by the modification suggested by Tuson and Neison.*

Chapman Jones† has further modified the process so as to make it easier to detect the end-point, and says of the method as worked by Tuson and Neison: "Their general method consists in dissolving the mercury compound in acid, as may be convenient, adding a little ammonium chloride, and then potassium carbonate, until an opalescent precipitate appears. The cyanide solution is then added. They give experiments showing the trustworthiness of the process as applied to the nitrate, sulphate, acetate, oxalate, sebate, and citrate of mercury; and state that the presence of nitrates, sulphates, chlorides, acetates, oxalates, citrates, and butyrates of potassium, sodium, calcium, and magnesium, and organic matter as far as tested, does not interfere with the accuracy of the method.

From my experience, I cannot affirm that these methods of working are satisfactory. There is considerable uncertainty as to the end of the reaction, because less potassium cyanide will effect a clearance if longer time is allowed.

These difficulties and uncertainties can, I find, be entirely eliminated, and the process reduced to a series of operations which are comparatively simple and rapid, by performing the titration in an entirely different manner from either variation suggested by the authors referred to. I employ a solution of mercuric chloride containing 0·01 gm. of metal per c.c., and a solution of crystallized potassium cyanide made by dissolving 7 gm. to the litre, the exact value of which is found by titrating it against the mercury solution. Strong ammonia diluted to ten times its bulk, and some diluted to fifty or a hundred times its bulk, are convenient.

Method of Procedure: If the mercury solution is not fit for titration, the metal is precipitated as sulphide, which, after washing, is washed off the filter and allowed to subside; the clear water is then decanted off, and *aqua regia* added to the moist residue. The precipitate, with the paper it is on, might doubtless be treated direct with *aqua regia*, as Tuson and Neison found that organic matter, so far as they tried it, does not influence the result. To avoid the possibility of volatilizing the mercury salt, the *aqua regia* is allowed to act in the cold. In a few hours, sometimes in far less time, the residue is of a pale

* *J. C. S.* 1877, 679. † *J. C. S.* **61**, 364.

yellow colour, and the solution may be diluted and filtered. The solution, or an aliquot part of it, is then coloured distinctly with litmus, treated with successive small quantities of powdered potassium carbonate until alkaline, warming but slightly, and then rendered just acid with dilute hydrochloric acid, with subsequent boiling to remove the CO_2. The mercury is not precipitated at all, unless the CO_2 is boiled out before acidification. After cooling, the dilutest ammonia mentioned above is added, a drop at a time, until the litmus in the solution shows that the excess of acid is very slight, or in just insufficient quantity to produce a permanent precipitate. A quantity of cyanide solution, which is known to be in excess of that required, is added, and, as a guide for the first titration, the ammonia may be added until a slight precipitate is produced, and cyanide until the solution is cleared. Two or three drops (not more) of the 1 in 10 ammonia are introduced, and then more of the mercury solution is added until the permanent turbidity produced matches that obtained by adding 0·1 c.c. of the mercury solution to about the same bulk of water as the test, and containing approximately the same amounts of litmus and free ammonia. Each drop of the mercury solution added produces its maximum turbidity in a few seconds, and it can be seen at a glance, if the flasks are properly placed, whether this turbidity is equal to or less than the standard. In a few seconds more it is quite obvious whether the turbidity is permanent or is growing less. Too much free ammonia causes the precipitate to clot together, and so vitiates the result. The presence of the litmus tends, in my experience, to lessen the error due to the variation in the state of aggregation of the precipitate when too much ammonia has been added. The turbidities so obtained will remain apparently unchanged for many hours. The 0·1 c.c. excess of mercury solution is of course allowed for in the calculation."

Acidimetric Cyanide Method (Rupp)*.—The solution of the mercuric salt is made neutral by the addition of alkali chloride, followed by phenolphthalein and sufficient alkali to just redden the solution, and then an execss of $^N/_4$ or $^N/_2$ potassium cyanide, sufficient to produce an intense red colour, is added, and the excess over that necessary to form mercuric cyanide is titrated with $^N/_1$ or $^N/_5$ hydrochloric or sulphuric acid, using methyl orange as indicator. For mercuric chloride, direct titration with potassium cyanide and phenolphthalein is allowable, but in solutions containing much alkali chloride, as obtained with mercuric nitrate and sulphate, the indirect method given above is to be preferred. In order to apply the method to mercuric cyanide, potassium iodide is added, so as to form the compound, K_2HgI_4, and liberate potassium cyanide, which is then titrated as above. Mercuric oxide may be dissolved in potassium iodide solution by shaking and the potassium hydroxide formed directly titrated with acid, using methyl orange as indicator.

6. Thiocyanate Method.†

This may be carried out as for silver salts, see p. 145. It is inapplicable when chlorides, mercurous salts, and nitrous acid are present. It is especially applicable in the presence of nitric acid and heavy metals. Rupp and Nöll‡ have adapted it to the valuation of organic mercury compounds thus :—

METHOD OF PROCEDURE: In order to oxidize the organic matter, 0·3 gm. of the substance is heated in a 150 c.c. flask with 4 gm. of potassium sulphate and 5 c.c. of concentrated sulphuric acid to gentle boiling until quite clear. A reflux tube, 40-50 cm. long is provided to prevent loss of mercury sulphate by volatilization, and this is then rinsed with 5-10 c.c. of concentrated sulphuric acid and removed; 0·1–0·2 gm. of potassium permanganate is now added to ensure the mercury being in the mercuric condition, and the heating continued until the pink colour vanishes. After cooling, the liquid is diluted to about 100 c.c., again allowed to cool, 2 c.c. of 10 per cent. iron alum solution added as indicator, and then titrated with $^N/_{10}$ thiocyanate, the flask being frequently rotated.

1 c.c. $^N/_{10}$ thiocyanate =0·010015 gm. Hg.

* *Chem. Zeit.* 1908, **32**, 1077. † *Ber.*, **35**, 2015. ‡ *Arch. Pharm.*, 1905, **243**, 1–5.

NICKEL.

The best method for the determination of this metal volumetrically is that of T. Moore,* whose description of the method is as follows :—

"If to an ammoniacal solution of nickel containing AgI in suspension (silver iodide being almost insoluble in weak ammonia) there is added potassium cyanide, the solution will remain turbid so long as all the nickel is not converted into the double cyanide of nickel and potassium, the slightest excess of cyanide being indicated by the clearing up of the liquid, and furthermore, this excess may be exactly determined by adding a solution of silver until the turbidity is reproduced. It is a fortunate circumstance that the complicated side-reactions existing in Parkes's copper assay do not appear to take place with nickel solutions, at least not when the temperature is kept below 20° C. This is fully borne out by the fact that the cyanide may be standardized on either silver or nickel solutions with equal exactness. In practice it has been found best to proceed in the following manner :—

Standard solution of silver nitrate, containing about 3 gm. of silver per litre. The strength of this solution must be accurately known.

Potassium iodide, 10 per cent. solution.

Potassium cyanide, 22 to 25 gm. per litre. This solution must be tested every few days, owing to its liability to change.

Standardizing the Cyanide Solution.—This may be accomplished in two ways; (*a*) on a solution of nickel of known metallic content, or (*b*) on the silver solution.

(*a*) First, accurately establish the relation of the cyanide to the silver solution, by running into a beaker 3 or 4 c.c. of the former; dilute this with about 150 c.c. of water, render slightly alkaline with ammonia, and then add a few drops of the potassium iodide. Now carefully run in the silver solution until a faint permanent opalescence is produced, which is finally caused to disappear by the further addition of a mere trace of cyanide. The respective volumes of the silver and cyanide solutions are then read off, and the equivalent in cyanide of 1 c.c. silver solution calculated. A solution containing a known quantity of nickel is now required. This must have sufficient free acid present to prevent the formation of any precipitate on the subsequent addition of ammonia to alkaline reaction; if this is not so, a little ammonium chloride may be added. A carefully measured quantity of the solution is then taken, containing about 0·1 gm. of nickel, and rendered distinctly alkaline with ammonia, a few drops of iodide added, and the liquid diluted to 150 or 200 c.c. A few drops of the silver solution are now run in, and the solution stirred to produce a uniform turbidity. The solution is now ready to be titrated with the cyanide, which is added slowly and with constant stirring until the precipitate wholly disappears; a few extra drops are added, after which the beaker is placed under the silver nitrate burette, and this solution gently dropped in until a faint permanent turbidity is again visible; this is now finally caused to dissolve by the mere fraction of a drop of the cyanide. A correction must now be applied for the excess of the cyanide added, by noting the amount of silver employed, and working out its value in cyanide from the data already found; this excess must then be deducted, the corrected number of c.c. being then noted as equivalent to the amount of nickel employed.

* *C. N.* **72**, 92.

(*b*) Having determined the relative value of the cyanide to the silver solution, and knowing accurately the metallic content of the latter, then Ag $\times 0{\cdot}272$ gives the nickel equivalent. This method is quite as accurate as the direct titration.

A modification of the above process, wherein one burette only is necessary, has been found very convenient, and has given most excellent results. It is as follows :—

When a solution of potassium cyanide, containing a small quantity of silver cyanide dissolved in it, is added to an ammoniacal solution of nickel containing potassium iodide, it is seen that silver iodide is precipitated, and the turbidity thus caused in the solution continues to increase up to the point where the formation of the nickel-potassium cyanide is complete ; any further addition after this stage is reached will produce a clearing up of the liquid, until, at last, the addition of a single drop causes the precipitate to vanish. This final disappearance is most distinct, and leaves no room for doubt. Such a solution may be prepared by dissolving 20 to 25 gm. of potassium cyanide in a litre of water, adding to this about 0·25 gm. silver nitrate, previously dissolved in a little water. For large quantities of nickel the quantity of silver may advantageously be diminished, and *vice versâ*. The value of the cyanide is best ascertained, in the manner already described, on a nickel solution.

Small quantities of cobalt do not seriously affect the results, but it must be remembered that it will be reckoned with the nickel ; its presence is at once detected by the darkening of the solution. Manganese or copper, when present, render the process valueless, so also does zinc ; the latter, however, in alkali pyrophosphate solution exercises no influence. In the presence of alumina, magnesia, or ferric oxide, citric acid, tartaric acid, or pyrophosphate of soda may be employed to keep them in solution. The action of iron is somewhat deceptive, as the solution, once cleared up, often becomes turbid again on standing for a minute : should this occur, a further addition of cyanide must be made until the liquid is rendered perfectly clear. The temperature of the solution should not much exceed 20° C. : above this the results become irregular. The amount of free ammonia has also a disturbing influence ; a large excess hinders or entirely prevents the reaction ; the liquid should, therefore, be only slightly, but very distinctly, alkaline. A word of caution must be given regarding the potassium cyanide, as many of the reputed pure samples are very far from being so. The most harmful impurity is, however, sulphur, as it gives rise to a darkening of the solution, owing to the formation of the less readily soluble silver sulphide ; to get rid of the sulphur impurity it is necessary to thoroughly agitate the cyanide liquor with oxide of lead, or, what is far preferable, oxide of bismuth.

As regards the exactness of the methods, it may be said that, after a prolonged experience, extending over many thousands of determinations, they have been found to be more accurate and reliable than either the electrolytic or gravimetric methods, and when time is a consideration the superiority is still more pronounced. The employment of organic acids or sodium pyrophosphate in the case when iron, zinc, etc., are present, allows the operator to dispense with the tedious separation which their presence otherwise

entails; and this is a matter of considerable importance in the assay of nickel mattes or German silver."

Another modification of this method has been adopted by the author for nickel ores existing in New Caledonia which contain iron, manganese, etc.

METHOD OF PROCEDURE: Two solutions are prepared: (*a*) 11 gm. of 98 per cent. potassium cyanide, 0·5 gm. of silver nitrate, and 1 litre of distilled water; and (*b*) 50 gm. of citric acid, 38 gm. (approximately) of sodium carbonate, 7·5 gm. of potassium iodide, and 500 c.c. of distilled water; 35 gm. of the sodium carbonate are first added, and then the remainder, decigram by decigram, until neutrality is attained, before adding the potassium iodide. It is important that solution *b* be either absolutely neutral or only very slightly alkaline. 2·5 gm. of the ore (after drying at 100° C) are placed in a 250 c.c. flask, dissolved in 20 c.c. of HCl, and the solution made up to 250 c.c. with water, and then well agitated. The insoluble silica, etc., is then filtered off, and to 50 c.c. of the filtrate 10 c.c. of solution *b* are added, then dilute ammonia in slight excess till the characteristic blue colouration is produced, and the solution is cooled. The liquid is then titrated with solution *a*, added gradually and with stirring. A white, cloudy precipitate forms at first, but disappears on the addition of the last drop of solution *a*. A standard solution of pure nickel is prepared and titrated in the same manner as the ore.

The process takes about thirty minutes, and the results, although usually a little too high, are very concordant. The method is not applicable to ores containing large quantities of iron, manganese, or cobalt, 25 per cent. being the limit for iron and manganese, and 1 per cent. for cobalt.

Jamieson* has recently published the following modification of the above process for the determination of **nickel in steel**:—

Dissolve 0·5 gm. of borings in 10 c.c. dilute nitric acid (1 : 1) in a 150 c.c. flask, according to the directions given for the ferrocyanide method. If the metal contains more than 0·5 % of manganese, remove it according to the same directions. Add to the nitric acid solution 2–3 gm. citric acid and 2 gm. anhydrous sodium pyrophosphate, then add ammonia slowly with stirring until the precipitate at first formed just dissolves and the solution acquires a very faint odour of ammonia. If too much ammonia has been used, it must be nearly neutralized by the careful addition of nitric acid. Dilute to about 150 c.c. and cool to a temperature below 20°, add a few drops of a 10 % solution of KI and enough $^{N}/_{10}$ silver nitrate solution—the volume of which must be noted—to produce a distinct turbidity. Then run in KCy solution very slowly with stirring until the turbidity just disappears, and the solution lightens to a golden-yellow colour. The solution should remain bright for five minutes, otherwise the titration is incomplete. Sometimes it happens that the turbidity disappears when only one-third to one-half of the required amount of cyanide has been used, but in this case on the addition of a drop or two of silver nitrate, or on waiting a moment, the turbidity reappears. The end-point is best observed when the beaker is placed on a white paper having an elliptical hole in it under which is placed a black glazed paper for contrast. In making the calculation the proper deduction for the silver nitrate used should be made.

The potassium cyanide solution should be standardized by means of the $^{N}/_{10}$ silver nitrate. To do this, pipette 20 c.c. into a beaker, dilute to about 150 c.c. with cold water, add ammonia until the odour is distinct but slight, add a few drops of 10 % KI solution, run in silver nitrate until a distinct turbidity is produced, and then finish by slowly adding the cyanide solution until the turbidity just disappears. The theoretical amount of nickel per c.c. of $^{N}/_{10}$ solution is 0·002934 gm., but instead of using this value it is perhaps preferable to standardize the solution with a steel of known content of nickel.

* *C.N.* 1910, **102**, 51.

Nickel-plating Solutions.—These contain, as a rule, only nickel sulphate and ammonia, and the nickel can be determined with a simple solution of potassium cyanide previously standardized on pure nickel ammonium sulphate. The nickel solution to be tested should be fairly concentrated and rendered feebly alkaline with ammonia. If there is iron present some ammonium tartrate should be added to prevent the precipitation of it by the ammonia. The cyanide is used in small quantities with constant shaking until a drop produces a clear yellowish solution. Copper, zinc, and cobalt must not be present.

Determination of Nickel and Cobalt by Potassium Ferrocyanide.—Standard K_4FeCy_6 – 20 gm. of the cryst. salt per litre (1 c.c. = about 0·003 gm. Ni or Co).

This method is referred to by Cantoni and Rosenstein* and is described in detail by Jamieson†; it is applicable for the determination of nickel and cobalt, but cannot be used in the presence of copper, zinc and manganese. The following procedure is recommended by Jamieson for standardizing the ferrocyanide solution, a similar course being pursued with the nickel or cobalt solution to be tested :—

A solution of nickel or cobalt is made from a pure salt and of known strength. Three equal portions, each containing about 0·1 gm. of the metal, are measured into beakers. 10 c.c. of a 10 % solution of ferric chloride and 2—3 gm. of citric acid are added to each, and then ammonia with stirring until the liquid has a faint smell of the reagent—a large excess being carefully avoided. The solutions are then diluted to about 100 c.c. with hot water and brought to a temperature of 63—75° C. The ferrocyanide is then run in *slowly* from a burette with constant stirring. A drop of the solution is from time to time transferred to a paraffined white plate and acidified with a drop of dilute acetic acid. The titration is finished when a greenish colour appears after five minutes' standing. The first portion is used to get an approximate result; the exact end-point being determined in the other two.

Determination of Nickel in Steel.—Dissolve 1 gm. of the borings in 10—15 c.c. dilute nitric acid (1 : 1) in a 150 c.c. flask covered with an inverted crucible cover. When the first violent action is over, remove cover, and boil gently with constant motion over a bunsen flame till the steel is dissolved, adding, if necessary, a few drops of strong HCl or a crystal of $KClO_3$ to complete solution. Now add 10 c.c. of conc. HNO_3, heat to boiling again, and add 0·5 gm. $KClO_3$. Boil off the chlorine, then add another 0·5 gm. of chlorate, and boil for two minutes. Allow the flask to cool a little and filter off the MnO_2 on a Gooch crucible, and wash with as small a quantity of cold water as possible. Then proceed according to the method described above. As the presence of a large amount of iron somewhat retards the appearance of the end-reaction, the ferrocyanide solution used should be standardized in the presence of about the same amount of iron as is contained in 1 gm. of steel. The results are accurate.

Determination of Cobalt and Nickel (Rupp and Pfennig)‡.

Cobalt.—The following method is based on the formation of a double cyanide, which is decomposed by excess of cobalt ions with formation of insoluble cobalt cyanide. 1 atom of cobalt was found to correspond to 5 molecules of KCN.

The cobalt solution, which must be neutral and contain between 0·02 and 0·75 % of cobalt, is run from a burette into a measured volume (5–25 c.c.) of $^N/_2$ potassium cyanide (undiluted) until a permanent brownish turbidity is produced.

$$1 \text{ c.c. } ^N/_2 \text{ KCN} = 0{\cdot}0059 \text{ gm. cobalt.}$$

$^N/_2$ KCN prepared from pure cyanide can be standardized by $^N/_4$ or $^N/_2$ HCl or H_2SO_4 using methyl orange as indicator.

* The *Analyst*, 1908, **33**, 107. † *C.N.* 1910, **102**, 51.

‡ *Chem. Zeit.* 1910, **34**, 322, and *J. S. C. I.* 1910, **29**, 518.

Nickel.—Exactly the same procedure is followed with regard to nickel. The neutral solution, diluted to contain 0·4–1·0 % nickel, is run into 10 c.c. of $^N/_2$ cyanide until a **permanent** turbidity is seen. Before commencing the titration 5–20 drops of 10 % ammonia should be added to the cyanide solution, as an increased sharpness of the end-reaction is thus secured: the addition of more than 5 c.c. however, leads to very erroneous results.

1 c.c. $^N/_2$ KCN = 0·007335 gm. Ni.

The method may also be carried out in the reverse way—for nickel, but not for cobalt—as follows: To the (neutral) nickel solution add 10 drops of a 1 % phenolphthalein solution, then run in $^N/_2$ cyanide from a burette until the precipitate formed is redissolved and a red tint obtained, showing the formation of the double cyanide. The addition of one drop more causes the formation of the usual red colour.

Another modification, also applicable to nickel only, is as follows: To the neutral nickel solution is added a measured quantity of cyanide, more than sufficient to form the double cyanide, and the excess determined by titration with $^N/_2$ HCl or H_2SO_4, using methyl orange as indicator.

NITROGEN AS NITRATES AND NITRITES.

Nitric Anhydride.

$N_2O_5 = 108·02.$

Nitrous Anhydride.

$N_2O_3 = 76·02.$

Normal acid	×	$0·0540 = N_2O_5$
Ditto	×	$0·1011 = KNO_3$
Metallic iron	×	$0·3761 = HNO_3$
Ditto	×	$0·6035 = KNO_3$
Ditto	×	$0·3224 = N_2O_5$

THE accurate determination of nitric acid in combination presents great difficulties, and can only be made by indirect means; the methods here given are sufficient for most purposes. Very few of them can be said to be simple, but it is to be feared that no simple process can ever be obtained for the determination of nitric acid in many of its combinations.

1. Determination by conversion into Ammonia (Schulze and Vernon Harcourt).

This method is based on the fact that when a nitrate is heated with a strong alkaline solution, and zinc added, ammonia is evolved; when zinc alone is used, however, the quantity of ammonia liberated is not a constant measure of the nitric acid present. Vernon Harcourt and Siewart* appear to have arrived independently at the result that by using a mixture of zinc and iron the reaction became quantitative.

A convenient form of apparatus is shown in fig. 47.

* *J. C. S.* 1862, 381; *An. Chem. u. Phar.* **125**, 293.

METHOD OF PROCEDURE : The distilling flask holds about 200 c.c. and is closely connected by a bent tube with another smaller flask, in such a manner that both may be placed obliquely upon a sand-bath, the bulb of the smaller flask coming just under the neck of the larger. The oblique direction prevents the spirting of the boiling liquids from entering the exit tubes, but as a further precaution these latter are in both flasks turned into the form of a hook ; from the second flask, which must be somewhat wide in the mouth, a long tube passes through a Liebig's condenser (which may be made of wide glass tube) into an ordinary tubulated receiver, containing normal sulphuric acid coloured with an indicator. The end of the distilling tube reaches to about the middle of the receiver, through the tubulure of which Harcourt passes a bulb apparatus of peculiar form, containing also coloured normal acid ; instead of this latter, however, a chloride of calcium

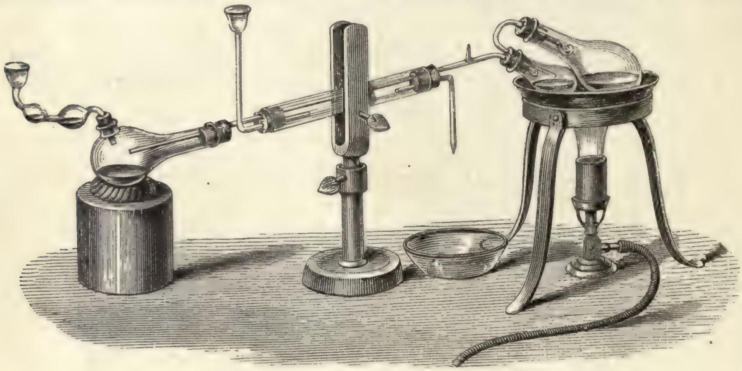


Fig. 47.

tube, filled with broken glass, and moistened with acid, will answer the purpose. The distilling tube should be cut at about two inches from the cork of the second flask, and connected by means of a well-fitting vulcanized tube ; by this means water may be passed through the tube when the distillation is over so as to remove any traces of ammonia which may have been retained on its sides. All the corks of the apparatus should be soaked in hot paraffin, so as to fill up the pores.

All being ready, about 50 gm. of finely granulated zinc (best made by pouring molten zinc into a warm iron mortar while the pestle is rapidly being rubbed round) are put into the larger flask with about half the quantity of clean iron filings which have been ignited in a covered crucible (fresh iron and zinc should be used for each analysis) ; the weighed nitrate is then introduced, either in solution, or with water in sufficient quantity to dissolve it, strong solution of caustic potash added, and the flask immediately connected with the apparatus, and placed on a small sand-bath, which can be heated by a gas-burner, a little water being previously put into the second flask. Convenient proportions of material are ½ gm. nitre, and about 25 c.c. each of water and solution of potash of spec. grav. 1·3. The mixture should be allowed to remain at ordinary temperature for about an hour (Eder).

Heat is now applied to that part of the sand-bath immediately beneath the larger flask, and the mixture is gradually raised to the boiling point. When distillation has actually commenced, the water in the second flask is made to boil gently ; by this arrangement the fluid is twice distilled, and any traces of fixed alkali which may have escaped the first are sure to be retained in the second flask. The distillation with the quantities above named will occupy about an hour and a half, and is completed when hydrogen is pretty freely liberated as the potash becomes concentrated. The lamp is then removed, and the whole allowed to cool, the distilling tube rinsed into the receiver, also the tube containing broken glass ; the contents of the receiver are then titrated with $^{N}/_{10}$ caustic potash or soda as usual.

Eder recommends that an ordinary retort, with its neck set upwards, should

be used instead of the flask for holding the nitrate, and that an aspirator should be attached to the exit tube, so that a current of air may be drawn through during and after the distillation.

Chlorides and sulphates do not interfere with the process.

This method is simplified in some agricultural experiment stations for the analysis of sodium and potassium nitrates.

METHOD OF PROCEDURE: 0·5 gm. of the nitrate is dissolved in about 50 c.c. of water in a convenient flask fitted with a bulb distilling tube such as is shown in either fig. 29 or 30. To the liquid is added about 5 gm. each of zinc dust and iron filings, then 80 c.c. of sodium hydrate solution (sp. gr. 1·3). The mixture is allowed to stand at ordinary temperature for an hour, when the distillation is commenced by heating up carefully and distilling until at least 100 c.c. are received into standard acid through a condenser, as in the Kjeldahl process.

Schmitt has suggested a further modification of this method, technically useful for mixed manures.

METHOD OF PROCEDURE: About 1 gm. of the substance in which the nitrate is to be determined is dissolved in water, 5 c.c. of glacial acetic acid and 3 gm. of a mixture of equal weights of finely powdered iron and zinc added, and the flask gently heated for 10 or 15 minutes. When cooled, 25 c.c. of sulphuric acid are cautiously added and a little solid paraffin to prevent frothing The flask is then gently heated to drive off the acetic acid, and the residue boiled as in the Kjeldahl method until colourless. Caustic soda in excess is then added and the distillation commenced in the usual way, receiving the distillate into standard acid. (See p. 87).

2. By Oxidation of Ferrous Salts (Pelouze).

(Not available in the presence of Organic Matter.)

The principle upon which this well-known process is based is as follows :—

(*a*) When a nitrate is brought into contact with a solution of ferrous oxide, mixed with free hydrochloric acid, and heated, part of the oxygen contained in the nitric acid passes over to the iron, forming a persalt, while the base combines with hydrochloric acid, and nitric oxide (NO) is set free. 3 eq. iron (=167·55) are oxidized by 1 eq. nitric acid(=63·02). If, therefore, a weighed quantity of the nitrate be mixed with an acid solution of ferrous chloride or sulphate of known strength in excess, and the solution boiled to expel the liberated nitric oxide, then the amount of unoxidized iron remaining in the mixture being found by a suitable method of titration, the quantity of iron converted from the ferrous into the ferric state will be the measure of the original nitric acid in the proportion of 167·55 to 63·02; or by dividing 63·02 by 167·55 the factor 0·3761 is obtained, so that if the amount of iron changed as described be multiplied by this factor, the product will be the amount of nitric acid present.

This method, though theoretically perfect, is in practice liable to serious errors, owing to the readiness with which a solution of a ferrous salt absorbs oxygen from the atmosphere. On this

account accurate results are only obtained by conducting hydrogen or carbon dioxide through the apparatus while the boiling is being carried on. This modification has been adopted by Fresenius with very satisfactory results.

The boiling vessel may consist of a small tubulated retort, supported in such a manner that its neck inclines upward ; a cork is fitted into the tubulure, and through it is passed a small tube connected with a vessel for generating either carbonic acid or hydrogen. If a weighed quantity of pure metallic iron is used for preparing the solution, the washed carbonic acid or hydrogen should be passed through the apparatus while it is being dissolved ; the solution so obtained, or one of double sulphate of iron and ammonia of known strength, being already in the retort, the nitrate is carefully introduced, and the mixture heated gently by a small lamp, or by the water bath, for ten minutes or so, then boiled until the dark-red colour of the liquid disappears and gives place to the brownish-yellow of ferric compounds. The retort is then allowed to cool, the current of carbonic acid or hydrogen still being kept up, then the liquid diluted freely, and titrated with $^{N}/_{10}$ permanganate.

Owing to the irregularities attending the use of permanganate with hydrochloric acid, it is preferable, in case this acid has been used, to dilute the solution less, and titrate with dichromate. Two grams of pure iron, or its equivalent in double iron salt, 0·5 gm. of saltpetre, and about 60 c.c. of strong hydrochloric acid, are convenient proportions for the analysis.

Eder* has modified Fresenius's improvements as follows :—

1·5 gm. of very thin iron wire is dissolved in 30 to 40 c.c. of pure fuming hydrochloric acid, placed in a retort of about 200 c.c. capacity ; the neck of the retort points upwards, at a moderately acute angle, and is connected with a U-tube, which contains water. Solution of the iron is hastened by applying a small flame to the retort. Throughout the entire process a stream of CO_2 is passed through the apparatus. When the iron is all dissolved the solution is allowed to cool, the stream of CO_2 being maintained ; the weighed quantity of nitrate contained in a small glass tube (equal to about 0·2 gm. HNO_3) is then quickly passed into the retort through the neck ; the heating is continued under the same conditions as before, until the liquid assumes the colour of ferric chloride. The whole is allowed to cool in a stream of CO_2 ; water is added in quantity, and the unoxidized iron is determined by titration with permanganate. The results are exceedingly good.

If the CO_2 be generated in a flask, with a tube passing downwards for the reception of the acid, air always finds its way into the retort, and the results are unsatisfactory. Eder recommends the use of Kipp's CO_2 apparatus. By carrying out the operation exactly as is now to be described, he has obtained very good results with ferrous sulphate in place of chloride.

The same apparatus is employed ; the tube through which CO_2 enters the retort passes to the bottom of the liquid therein, and the lower extremity of this tube is drawn out to a fine point. The bubbles of CO_2 are thus reduced in size, and the whole of the nitric acid is removed from the liquid by the passage of these bubbles. The iron wire is dissolved in excess of dilute sulphuric acid (strength 1 : 3 or 1 : 4). When the liquid in the retort has become cold, a small tube containing the nitrate is quickly passed, by means of a piece of platinum wire attached to it, through the tubulus of the retort, and the cork is replaced before

* *Z. a. C.* **16**, 267.

the tube has touched the liquid; CO_2 is again passed through the apparatus for some time, after which, by slightly loosening the cork, the tube containing the nitrate is allowed to fall into the liquid. The whole is allowed to remain at the ordinary temperature for about an hour—this is essential—after which time the contents of the retort are heated to boiling, CO_2 being passed continuously into the retort, and the boiling continued till the liquid assumes the light yellow colour of ferric sulphate. After cooling, water is added (this may be omitted with dichromate), and the unoxidized iron is determined by permanganate.

Eder also describes a slight modification of this process, allowing of the use of a flask in place of the retort, and of ammonio-ferrous sulphate in place of iron wire. Although the titration with permanganate is more trustworthy when sulphuric acid is employed than when hydrochloric acid is used, he nevertheless thinks that the use of ferrous chloride is generally to be recommended in preference to that of ferrous sulphate. When the chloride is employed, no special concentration of acid is necessary; the nitric oxide is more readily expelled from the liquid, and the process is finished in a shorter time. Some magnesium sulphate should, however, be used to prevent the disturbing effect of HCl when permanganate is used for titration.

The final point in the titration with permanganate, when the sulphate is employed, is rendered more easy of determination by adding a little potassium sulphate to the liquid.

(*b*) **Direct titration of the resulting Ferric salt by Stannous Chloride.**—Fresenius has adopted the use of stannous chloride for titrating the ferric salt with very good results.

The following plan of procedure is recommended by the same authority.

A solution of ferrous sulphate is prepared by dissolving 100 gm. of the crystals in 500 c.c. of hydrochloric acid of spec. grav. 1·10; when used for the analysis, the small proportion of ferric oxide invariably present in it is found by titrating with stannous chloride. The nitrate being weighed or measured, is brought together with 50 c.c. (more or less, according to the quantity of nitrate) of the iron solution into a long-necked flask, through the cork of which two glass tubes are passed, one connected with a CO_2 apparatus, and reaching to the middle of the flask, the other simply an outlet for the passage of the gas. When the gas has driven out all the air, the flask is at first gently heated, and eventually boiled, to dispel all the nitric oxide. The CO_2 tube is then rinsed into the flask, and the liquid, while still boiling hot, titrated for ferric chloride, as on p. 127.

The liquid must, however, be allowed to cool before titrating with iodine for the excess of stannous chloride. While cooling, the stream of CO_2 should still be continued. The quantity of iron changed into peroxide, multiplied by the factor 0·3761, will give the amount of nitric acid (HNO_3).

EXAMPLE: (1) A solution of stannous chloride was used for titrating 10 c.c. of solution of pure ferric chloride containing 0·2151 gm. Fe; 25·65 c.c. of tin solution were required, therefore that quantity was equal to 0·0809 gm. of HNO_3, or 0·06932 gm. of N_2O_5.

(2) 50 c.c. of acid ferrous sulphate were titrated with tin solution for ferric oxide, and 0·25 c.c. was required.

(3) 1 c.c. tin solution = 3·3 c.c. iodine solution.

(4) 0·2177 gm. of pure nitre was boiled, as described, with 50 c.c. of the acid ferrous sulphate, and required 45·05 c.c. tin solution, and 4·7 c.c. iodine—

4·7 c.c. iodine solution	$=1{\cdot}42$ c.c. $SnCl_2$
The peroxide in the protosulphate solution	$=0{\cdot}25$ c.c.
	1·67

$$45{\cdot}05 - 1{\cdot}67 = 43{\cdot}38$$
$$\therefore\ 25{\cdot}65 : 43{\cdot}38 = 0{\cdot}06932 : x$$
$$x = 0{\cdot}1172\ N_2O_5$$

instead of 0·1163, or 53·69 per cent. instead of 53·42. A mean of this and three other determinations, using varying proportions of tin and iron solutions, gave exactly 53·42 per cent. In the case of pure materials, therefore, the process is entirely satisfactory.

The above process is slightly modified by Eder. About 10 gm. of ammonium-ferrous sulphate are dissolved in a flask in about 50 c.c. of hydrochloric acid (sp. gr. 1·07) in a stream of CO_2. The tube through which the CO_2 enters is drawn to a point; an exit tube, somewhat trumpet-shaped, to admit of any liquid that may spirt finding its way back into the flask, passes downwards into water. After solution of the double salt, the nitrate is dropped in with the precautions already detailed, and the liquid is boiled until the nitric oxide is all expelled. The hot liquid is diluted with twice its own volume of water, excess of stannous chloride solution is run in, the whole is allowed to cool in a stream of CO_2, and the excess of tin is determined by means of standard iodine.

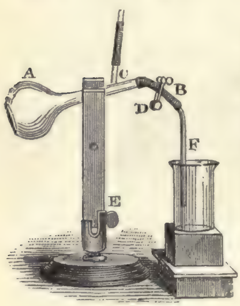


Fig. 48.

(*c*) **Holland's Modification of the Pelouze Process.**—The arrangement of apparatus shown in fig. 48 obviates the use of an atmosphere of H or CO_2. A is a long-necked assay flask drawn off at B, so as to form a shoulder, over which is passed a piece of stout pure india-rubber tube, D, about 6 centimetres long, the other end terminating in a glass tube, F, drawn off so as to leave only a small orifice. On the elastic connector D is placed a screw clamp. At C, a distance of 3 centimetres from the shoulder, is cemented with a blow-pipe a piece of glass tube about 2 centimetres long, surmounted by one of stout elastic tube, rather more than twice that length. The elastic tubes must be securely attached to the glass by binding with wire. After binding, it is as well to turn the end of the conductor back, and smear the inner surface with fused caoutchouc, and then replace it to render the joint air-tight.

Method of Procedure: A small funnel is inserted into the elastic tube at C, the clamp at D being for the time open; after the introduction of the solution, followed by a little water which washes all into the flask, the funnel is removed, and the flask supported, by means of the wooden clamp, in the inclined position it occupies in the figure. The contents are now made to boil so as to expel all air and reduce the volume of the fluid to about 4 or 5 c.c. When this point is

reached a piece of glass rod is inserted into the elastic tube at C, which causes the water vapour to escape through F.

Into the small beaker is put about 50 c.c. of a previously boiled solution of ferrous sulphate in hydrochloric acid (the amount of iron already existing in the ferric state must be known).

The boiling is still continued for a moment to ensure perfect expulsion of air from F, the lamp is then removed, and the caoutchouc connector slightly compressed with the first finger and thumb of the left hand. As the flask cools the solution of iron is drawn into it: when the whole has nearly receded the elastic tube is tightly compressed with the fingers, whilst the sides of the beaker are washed with a jet of boiled water, which is also allowed to pass into the flask. The washing may be repeated, taking care not to dilute more than is necessary or to admit air. Whilst F is still full of water, the elastic connector previously compressed with the fingers is now securely closed with the clamp, the screw of which is worked with the right hand. Provided the clamp is a good one, F will remain full of water during the subsequent digestion.

After heating in a water bath at 100° for half an hour, the flask is removed from the water bath and cautiously heated with a small flame, the fingers at the same time resting on the elastic connector at the point nearest the shoulder; as soon as the tube is felt to expand, owing to the pressure from within, the lamp is removed and the screw clamp released, the fingers maintaining a secure hold of the tube, the gas-flame is again replaced, and when the pressure on the tube is again felt, this latter is released altogether, thus admitting of the escape of the nitric oxide, through F, which should be below the surface of water in the beaker whilst these manipulations are performed. The contents of the flask are now boiled until the nitric oxide is entirely expelled, and the solution of iron shows only the brown colour of the perchloride. At the completion of the operation, the beaker is first removed, and then the lamp.

It now only remains to transfer the ferric solution to a suitable vessel and determine the perchloride with stannous chloride as in *b*.

A mean of six experiments for the percentage determination of N_2O_5 in pure nitre gave 53·53 per cent. instead of 53·42. The process is easy of execution, and gives satisfactory technical results. The point chiefly requiring attention is that the apparatus should be air-tight, which is secured by the use of good elastic tubes and clamp.

3. Schlösing's Method (available in the presence of Organic Matter).

The solution of nitrate is boiled in a flask till all air is expelled, then an acid solution of ferrous chloride drawn in, the mixture boiled, and the nitric oxide gas collected over mercury in a balloon filled with mercury and milk of lime; the gas is then brought, without loss, in contact with oxygen and water, so as to convert it again into nitric acid, then titrated with $^{N}/_{10}$ alkali as usual.

This method was devised by Schlösing for the determination of nitric acid in tobacco, and is especially suitable for that and similar purposes, where the presence of organic matter would interfere with the direct titration of the iron solution. Where the quantity of nitric acid is not below 0·15 gm. the process is fairly accurate, but needs a special and rather complicated arrangement of apparatus, the description of which may be found in Fresenius's *Quant. Anal.* sixth edition.

An arrangement of apparatus, dispensing with the use of mercury, has been devised by Wildt and Scheibe,* which simplifies the method and gives accurate results with not less than 0·25 gm. N_2O_5. With smaller quantities the results are too low. Fig. 49 shows the apparatus used.

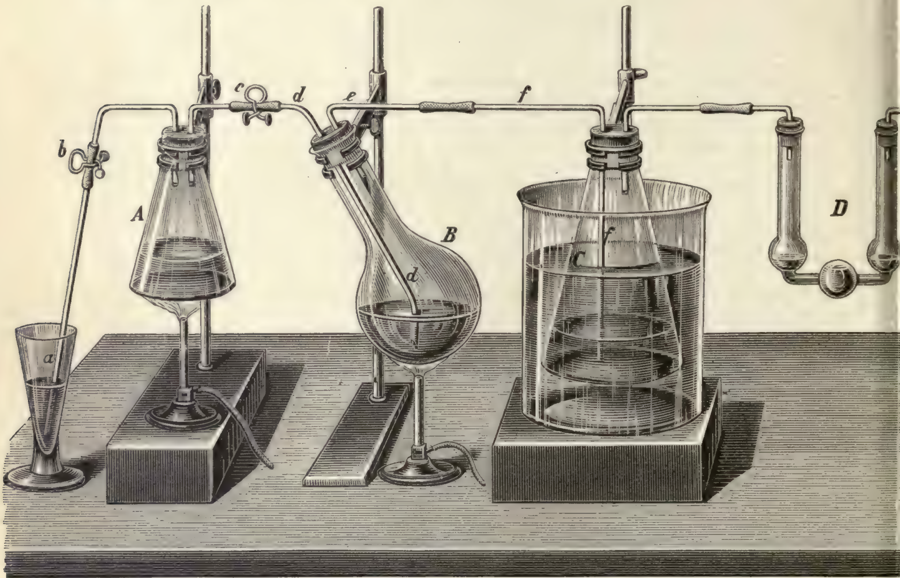


Fig. 49.

A is a conical flask of 250 c.c. capacity, containing the solution to be analysed. B is a round-bottomed flask of 250—300 c.c. capacity, half filled with caustic soda, to absorb any HCl which might be carried over from A. C is a conical flask of 750 c.c. capacity, containing a little water to absorb the nitric acid. D is a tube containing water to collect any nitric acid not absorbed by the water in C. The tube *d* is bent, as shown in the diagram, and drawn out to a point, to diminish the size of the bubbles. The tube *e* is wide, and cut obliquely to prevent water collecting and passing into C.

METHOD OF PROCEDURE: The clip *b* is closed and *c* opened, and the tube *e* disconnected from *f*. The solutions in A and B are then boiled for 20 minutes to remove all oxygen. The tubes *e* and *f* are again connected, the clip *c* is closed, the flame under B increased to prevent the liquid in C from being drawn back, and the clip *b* is opened. As soon as steam issues from the tube *a*, it is dipped into a conical glass containing 50 c.c. of ferrous chloride prepared according to Schlösing's directions,and the flame under A is removed, when the ferrous chloride enters the flask. The clip *b* is regulated with the finger and thumb, so as to prevent the entry of air into the flask. The conical vessel is rinsed two or three times with water, and this is allowed to enter the flask, and the clip *b* is then closed, and the vessel A heated. The liquid in A turns brown in a short time, and nitric oxide is evolved. The clip *c* is opened slightly from time to time

* *Z. a. C.* **23**, 151.

until the pressure is high enough, when it is opened entirely. The flames must be so regulated that a slow current of gas bubbles through the water in C. The hydrochloric acid is removed by the caustic soda in B, and the nitric oxide on coming in contact with the air in C is oxidized, and the nitric acid absorbed by the water. In case the current of gas is too rapid, the escaping nitric acid is absorbed in D. After an hour the tubes *e* and *f* are disconnected, while the solutions in A and B are still boiling, and the nitric acid is titrated with dilute caustic soda about ($\frac{1}{4}$ normal). The vessel C must be well cooled during the whole experiment, which occupies about an hour and a half.

Good results were obtained with nitrates of potash and soda, both alone and mixed with ammonium sulphate, superphosphate, and amido compounds. With superphosphate the solution should be made slightly alkaline, to prevent the liberation of nitric acid.

Warington* has made a series of experiments on the original Schlösing process, for the purpose of testing its accuracy when small quantities of nitric acid have to be determined in the presence of organic substances, such for instance as in soils, the sap of beetroot, etc.; but instead of re-converting the nitric oxide into nitric acid as in the original method, he collected the gas either over caustic soda, as recommended by Reichardt, or over mercury, and ascertained its amount by measurement in Frankland's gas apparatus. The results obtained by Warington plainly showed that even in the most favourable circumstances the method as usually worked in Germany, either by the alkalimetric titration or by measurement of the gas, invariably gave results much too low, especially if the quantity of nitrate operated on was small, say 5 or 6 centigrams of nitre; moreover, when sugar or similar organic substance was present the resulting gas was very impure, and the distillates were highly coloured from the presence of some volatile products. The nitric oxide also suffered considerable diminution of volume when left for any length of time in contact with the distillate, especially when over caustic soda. This being the case, the following modification originally recommended by Schlösing was adopted in which CO_2 was employed, both to assist in expelling the air from the apparatus, and to chase out the nitric oxide produced.

The form of apparatus adopted by Warington is shown in fig. 50. The vessel in which the reaction takes place is a small tubulated receiver, the tubulure of which has been bent near its extremity to make a convenient junction with the delivery tube, which dips into a trough of mercury on the left. The long supply tube attached to the receiver is of small bore, and is easily filled by a $\frac{1}{2}$ c.c. of liquid. The short tube to the right is also of small bore, and is connected by a caoutchouc tube and clamp with an apparatus for the continuous production of carbon dioxide.

In using this apparatus the supply tube is first filled with strong HCl, and CO_2 is passed through the apparatus till a portion of the gas collected in a jar over mercury is found to be entirely absorbed by caustic potash. The current of gas is then stopped by closing the clamp to the right. A chloride of calcium bath at 140° is next brought under the receiver, which is immersed one-half or more in the hot fluid; the temperature of the bath is maintained throughout the operation by a gas burner placed beneath it. By allowing a few drops of HCl to enter the hot receiver, the CO_2 it contains is almost entirely expelled. A jar filled with

* *J. C. S.* 1880, 468.

mercury is then placed over the end of the delivery tube, and all is ready for the commencement of a determination.

The nitrate, which should be in the form of a dry residue in a small beaker or basin, is dissolved in about 2 c.c.* of strong ferrous chloride solution, 1 c.c. of strong HCl is added, and the whole is then introduced into the receiver through the supply tube, being followed by successive rinsings with HCl, each rinsing not exceeding a ½ c.c., as the object is to introduce as small a bulk of liquid as possible.

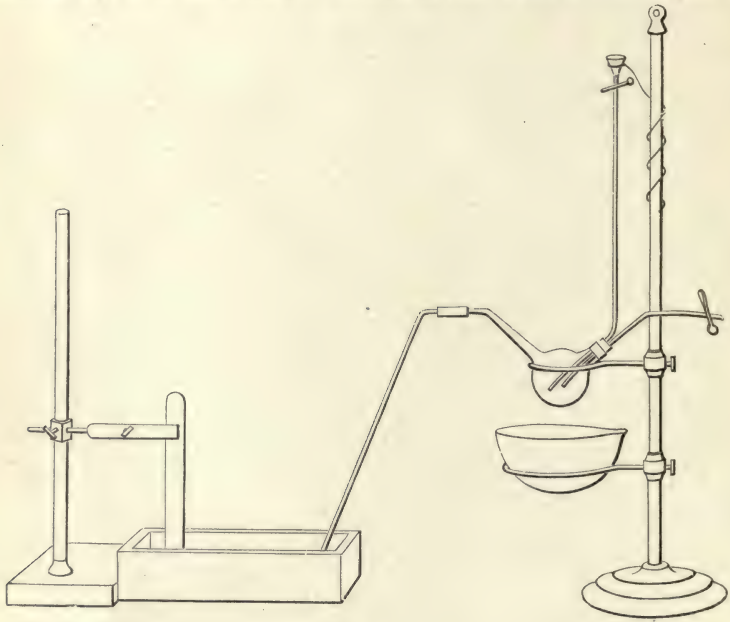


Fig. 50.

The contents of the receiver are in a few minutes boiled to dryness; a little CO_2 is admitted before dryness is reached, and again afterwards to drive over all remains of nitric oxide. If the gas is not to be analysed till next day, it is advisable to use more CO_2, so as to leave the nitric oxide diluted with several times its volume of that gas. As soon as one operation is concluded the apparatus is ready for another charge.

This mode of working presents the following advantages :—

(1) The volume of liquid introduced into the apparatus is much diminished, and with this of course the amount of dissolved air contributed from this source.

(2) By evaporation to dryness a complete reaction of the nitrate and ferrous chloride, and a perfect expulsion of the nitric oxide formed, is as far as possible attained.

(3) The nitric oxide in the collecting jar is left in contact with a much smaller volume of acid distillate, and its liability to absorption is greatly diminished by its dilution with CO_2.

The results obtained with this apparatus by Warington on small quantities of nitre alone, and when mixed with varying quantities of ammonium salts and organic substances including sugar, showed a marked improvement upon the method as usually carried out.

* Supposing the ferrous chloride to contain 2 gm. of iron per 10 c.c., then 1 c.c. of the solution will be nearly equivalent to 0·1207 gm. of nitre, or 0·0167 gm. of nitrogen. A considerable excess of iron should, however, always be used.

A further improvement has been made in this method by Warington,* and described by him as follows :—

The apparatus now employed is quite similar to that shown in fig. 50, with the only difference that the bulb retort in which the reaction takes place is now only 1¾ inch in diameter, thus more exactly resembling the form employed by Schlösing. A bulb of this size is sufficient for the analysis of soil extracts; for determinations of nitrates in vegetable extracts a larger bulb is required.

The chief improvement consists in the use of CO_2 as free as possible from oxygen. The generator is formed of two vessels. The lower one consists of a bottle with a tubulure in the side near the bottom; this bottle is supported in an inverted position, and contains the marble from which the gas is generated. The upper vessel consists of a similar bottle standing upright; this contains the HCl required to act on the marble. The two vessels are connected by a glass tube passing from the side tubulure of the upper vessel to the inverted mouth of the lower vessel; the acid from the upper vessel thus enters below the marble. CO_2 is generated and removed at pleasure by opening a stop-cock attached to the side tubulure of the lower vessel, thus allowing HCl to descend and come in contact with the marble. The fragments of marble used have been previously boiled in water. The boiling is conducted in a strong flask. After boiling has proceeded some time, a caoutchouc stopper is fixed in the neck of the flask, and the flame removed; boiling will then continue for some time in a partial vacuum. The lower reservoir is nearly filled with the boiled marble thus prepared. The HCl has been also well boiled, and before it is introduced into the upper reservoir it has dissolved in it a moderate quantity of cuprous chloride. As soon as the acid has been placed in the upper reservoir it is covered by a layer of oil. The apparatus being thus charged is at once set in active work by opening the stop-cock of the marble reservoir; the acid descends, enters the marble reservoir, and the CO_2 produced drives out the air which is necessarily present at starting. As the acid reservoir is kept on a higher level than the marble reservoir, the latter is always under internal pressure, and leakage of air from without cannot occur.

The presence of the cuprous chloride in the hydrochloric acid not only ensures the removal of dissolved oxygen, but affords an indication to the eye of the maintenance of this condition. So long as the acid rémains of an olive tint, oxygen will be absent; but should the acid become of a clear blue-green, it is no longer certainly free from oxygen, and more cuprous chloride must be added.

A further slight improvement adopted consists in the use of freshly-boiled reagents, which are employed in as small a quantity as possible. When boiling the hydrochloric acid it is well to add a few drops of ferrous chloride, in order more certainly to remove any dissolved oxygen.

The mode of operation is as follows :—The apparatus is fitted together, the long funnel tube attached to the bulb retort being filled with water. Connection is made with the glass stop-cock of the CO_2 generator by means of a short stout caoutchouc tube, provided with a pinch-cock. The pinch-cock being opened, the stop-cock is turned till a moderate stream of bubbles rises in the mercury trough; the stop-cock is left in this position, and the admission of gas is afterwards controlled by the pinch-cock, pressure on which allows a few bubbles to pass at a time. The heated chloride of calcium bath is next raised, so that the bulb retort is almost submerged; the temperature, shown by a thermometer which forms part of the apparatus, should be 130–140°. By boiling small quantities of water or hydrochloric acid in the bulb retort in a stream of CO_2 the air present is expelled; the supply of gas must be stopped before the boiling has ceased, so as to leave little in the retort. Previous to very delicate experiments it is advisable to introduce through the funnel tube a small quantity of nitre, ferrous chloride, and hydrochloric acid, rinsing the tube with the latter reagent; any trace of oxygen remaining in the apparatus is then consumed by the nitric oxide formed, and after boiling to dryness, and driving out the nitric oxide with CO_2, the apparatus is in a perfect condition for a quantitative experiment.

Soil extracts may be used without other preparation than concentration. Vegetable juices, which coagulate when heated, require to be boiled and filtered,

* *J. C. S.* 1882, 345.

or else evaporated to a thin syrup, treated with alcohol and filtered. A clear solution being thus obtained, it is concentrated over a water bath to the smallest volume, in a beaker of smallest size. As soon as cool, it is mixed with 1 c.c. of a cold saturated solution of ferrous chloride and 1 c.c. HCl, both reagents having been boiled and cooled immediately before use. In mixing with the reagents care must be taken that bubbles of air are not entangled ; this is especially apt to occur with viscid extracts. The quantity of ferrous chloride mentioned is amply sufficient for most soil extracts, but it is well perhaps to use 2 c.c. in the first experiment of a series ; the presence of a considerable excess of ferrous chloride in the retort is thus ensured. With bulky vegetable extracts more ferrous chloride should be employed ; to the syrup from 20 gm. of mangel sap should be added 5 c.c. of ferrous chloride, and 2 c.c. of hydrochloric acid.

The mixture of the extract with ferrous chloride and HCl is introduced through the funnel tube and rinsed in with three or four successive $\frac{1}{2}$ c.c. of HCl. The contents of the retort are then boiled to dryness, a little CO_2 being from time to time admitted, and a more considerable quantity used at the end to expel any remaining nitric oxide. The most convenient temperature is 140°, but in the case of vegetable extracts it is well to commence at 130°, as there is some risk of the contents of the retort frothing over. The gas is collected in a small jar over mercury. As soon as one operation is completed, the jar is replaced by another full of mercury, and the apparatus is ready to receive a fresh extract. A series of five determinations, with all the accompanying gas analyses, may be readily performed in one day. The bulb retort becomes encrusted with charcoal, when extracts rich in organic matter are the subject of analysis ; it is best cleaned first with water, and then by heating oil of vitriol in it.

Mercury, contrary to the statement in most text-books, is gradually attacked by hydrochloric acid in the presence of air ; the mercury in the trough is thus apt to become covered with a grey chloride, and it is quite necessary to keep the store of mercury in contact with sulphuric acid to preserve its mobile condition.

The gas analysis is of a simple character ; the gas is measured after absorption of the CO_2 by potash, and again after absorption of the nitric oxide, the difference giving the amount of this gas. For the absorption of nitric oxide, a saturated solution of ferrous chloride was for some time employed. This method is not, however, perfectly satisfactory when the highest accuracy is required, the nitric oxide being generally rather under-estimated, unless the process of absorption is repeated with a fresh portion of ferrous chloride. The error is greater in proportion to the quantity of unabsorbed gas present. Thus, with a mixture of nitrogen and nitric oxide containing little of the former absorption of the nitric oxide by successive treatment with oxygen and pyrogallol over potash showed 97·8 per cent. of nitric oxide ; while the same gas, analysed by a single absorption with ferrous chloride (after potash), showed 97·5 per cent. of nitric oxide. With a mixture containing more nitrogen, the oxygen method showed 65·9 per cent. of nitric oxide ; while one absorption with ferrous chloride gave 64·2 per cent., and a second absorption, in which the ferrous chloride was plainly discoloured, 66·2 per cent. The use of ferrous chloride as an absorbent for nitric oxide has now been given up, and the oxygen method substituted. All the measurements of the gas are now made without shifting the laboratory vessel ; the conditions are thus favourable to extreme accuracy.

The chief source of error attending the oxygen process lies in the small quantity of carbonic oxide produced during the absorption with pyrogallol ; this error becomes negligible if the oxygen is only used in small excess. The difficulty of using the oxygen in nicely regulated quantity may be removed by the use of Bischof's gas delivery-tube. This may be made of a test-tube, having a small perforation half an inch from the mouth. The tube is partly filled with oxygen over mercury, and its mouth is then closed by a finely-perforated stopper, made from a piece of wide tube, and fitted tightly into the test-tube by means of a covering of caoutchouc.

When this tube is inclined, the side perforation being downwards, the oxygen is discharged in small bubbles from the perforated stopper while mercury enters through the side opening. Using this tube, the supply of oxygen is perfectly under control, and can be stopped as soon as a fresh bubble ceases to produce a red tinge in the laboratory vessel. The trials made with this apparatus have been very satisfactory. If nitrites are to be determined by this method, it is necessary first to convert them into nitrates with excess of hydrogen peroxide, which is entirely destroyed by the subsequent evaporation to dryness.

4. By the Kjeldahl Process.

By the Gunning-Jodlbauer modified method described on p. 88 it is now quite possible to determine the nitrogen in commercial nitrates with great accuracy and very little personal attention.

5. Ulsch's Method.

This is a simple and ready plan of determining alkali nitrates, or the amount of them existing in manures when there is no salt of ammonia or other form of nitrogen present. It depends on the fact that when nitrate of soda or potash is boiled with dilute sulphuric acid, together with iron reduced by hydrogen, the nitrogen becomes converted into ammonium sulphate. The ammonia is then distilled off by boiling with caustic soda as in Kjeldahl's method.

METHOD OF PROCEDURE: 0·5 gm. of an alkali nitrate, dissolved in 25 c.c. of water, or a volume of manure solution containing about that quantity, which should not measure more than 25 or 30 c.c., is put into a small (150 c.c.) flask. 5 gm. of reduced iron and 20 c.c. of dilute sulphuric acid (1·3) are then added, and the flask placed in an inclined position and the reaction allowed to continue in the cold until effervescence ceases. The mixture is then boiled for six or seven minutes, and allowed to cool. The liquid is then transferred to a Kjeldahl distilling flask, an excess of caustic soda with a few pieces of zinc added, and the ammonia collected in standard acid and titrated as usual in the Kjeldahl process. The calculation into nitrogen or alkali nitrate presents no difficulty.

Some operators have obtained high results by this method, owing to the reduced iron containing some form of nitrogen or ammonia. A *blank* experiment should therefore be made with the iron used to find whether such impurity exists. Brandt found that cyanogen was the offending agent, and this was removed by ignition of the iron again in hydrogen.

The official method* to be used in the analysis of fertilizers under the Fertilizers and Feeding Stuffs Act, 1906, is as follows :—

NITROGEN IN NITRATES IN THE ABSENCE OF AMMONIUM SALTS AND OF ORGANIC NITROGEN.

1 gram of the sample shall be placed in a half-litre Erlenmeyer flask with 50 c.c. of water, 10 grams of reduced iron and 20 c.c. of sulphuric acid of 1·35 sp. gr.† shall be added. The flask shall be closed with a rubber stopper provided with

* The Fertilizers and Feeding Stuffs (Methods of Analysis) Regulations, 1908. No. 964.

† Made by mixing 1 vol. of 1·84 acid with 2 vols. of water.

a thistle tube, the head of which shall be half filled with glass beads. The liquid shall be boiled for five minutes, and the flask shall then be removed from the flame, any liquid that may have accumulated among the beads being rinsed back with water into the flask. The solution shall be boiled for three minutes more, and the beads again washed with a little water. The quantity of ammonia shall then be determined by distillation into standard acid after liberation with alkali. (Caustic Soda is generally used.)

6. Technical method for the Pelouze process with Alkali Nitrates and Nitrated Manures.

Wagner has arranged a simple form of the Schlösing method, which gives fairly good results and permits of rapid working.

The following is the slightly modified arrangement, as adopted at the Halle Agricultural Experiment Station, for the determination of nitrogen as nitrates in fertilizers.

A 250 c.c. flask is fitted with a two-hole rubber stopper. One hole carries an ordinary gas delivery-tube, and the other a thistle funnel, having a stop-cock below the funnel. The end of this tube is narrowed, and does not quite reach the liquid in the flask.

A solution of 200 gm. of iron wire in hydrochloric acid is made and diluted to 1 litre. 50 c.c. of this solution, and the same quantity of 10 % HCl, are placed in the flask, and the air expelled by boiling. 10 c.c. of a standard solution of pure sodium nitrate, containing 25 gm. per litre, are then placed in the funnel, and allowed gradually to drop into the boiling solution of iron. A gas tube graduated to 100 c.c. is filled with 40 % solution of caustic potash, and the nitric oxide collected in the usual way. When the nitre solution is nearly all dropped in, the funnel is filled with 10 per cent. HCl, and run down drop by drop, and when no more nitric oxide is evolved the tube containing the gas set aside in a large jar containing distilled water. 10 c.c. of the solution to be tested are now put into the funnel, taking care that not more than 100 c.c. of gas will result. The gas is collected as before in a fresh tube precisely as in the case of the pure nitrate. In this manner ten or twelve determinations can be made with one and the same ferrous solution. Finally, a fresh test is made with standard nitre solution; the readings of the tubes are taken, and as they will all be of the same temperature and pressure no correction is necessary, all being allowed to cool to the same point. The comparison between the pure nitrate and the sample will afford the calculation.

Technical use of the Pelouze Process for Mixed Manures.—Vincent Edwards* adopts the following method for manures containing nitrates together with ammonia and other matters. The solutions required are :—

Standard potassium dichromate, 14·742 gm. per litre. 1 c.c. = 0·0085 gm. $NaNO_3$ or 0·0101 gm. KNO_3.

Ferrous sulphate. 100 gm. of crystallized salt with 100 c.c. of concentrated H_2SO_4 per litre.

The exact working strength of these two solutions in practice is found by boiling 50 c.c. of the iron solution till it becomes thick in a stout well annealed glass flask, preferably of Jena glass, which is fitted with a Bunsen valve, made by cutting the rubber tube with a sharp razor, the glass tube to which it is fitted passing through a light fitting rubber stopper ; after boiling the flask is set aside to cool,

* *C. N.* **71**, 307.

then 100 c.c. or so of water are added, and the titration made with dichromate in the usual way with fresh solution of ferricyanide as indicator.

METHOD OF PROCEDURE: 10-20 gm. of the nitrated manure, according to its richness, are exhausted with water and the liquid made up to 200 c.c.

20 c.c. of this solution are placed in the boiling flask together with 50 c.c. of the iron solution, the stopper with valve is then inserted, and the mixture boiled until it becomes thick, and semi-solid drops are splashed against the sides of the flask; the flask is then enveloped in a cloth, and removed to cool; when cool, 100 c.c. or so of water are run into the flask, well shaken, then titrated with the dichromate as in the case of the blank experiment.

EXAMPLE: The blank titration showed that 50 c.c. of iron solution required 54 c.c. of dichromate. 20 c.c. of the manure solution (=1 gm. manure) were treated as above described, and required 31 c.c. of dichromate, therefore 54 − 31 = 23 c.c. which multiplied by 0·0085 = 0·1955 or 19·55 % of $NaNO_3$ in the manure. The manure was known to be a mixture of 20 % of nitrate of soda, of 95·5 % strength, with 80 per cent. of an ammoniacal guano.

This technical process is, of course, chiefly valuable where the nitrate is required to be determined apart from the ammonia.

7. Devarda's Method.*

The nitrate is reduced to ammonia by the evolution of hydrogen generated from alkali hydroxide and an alloy of aluminium with copper and zinc (Al 45, Cu 50, Zn 5), the ammonia being distilled into standard acid as in Kjeldahl's method. The alloy, which can be readily purchased, is brittle. It should be powdered sufficiently finely to pass through a No. 60 sieve, and five times the weight of the nitrate taken for the determination should be used. Cahen,† who has recently published results obtained with the method, distils the ammonia with steam, in preference to distillation by boiling.

METHOD OF PROCEDURE: About 0·5 gm. of the nitrate is dissolved in 110 c.c. of water in a Jena glass bulb flask, and 2-3 gm. of the alloy, 5 c.c. of alcohol, and 50 c.c. of caustic alkali (sp. gr. 1·3) added. The flask is then quickly connected to the Kjeldahl distilling apparatus and allowed to stand for 30 minutes, when the brisk reaction will be complete. The contents of the flask are then slowly raised to the boiling temperature, and steam passed for 30 minutes, when all the ammonia will have distilled over.

8. Gasometric Determination, as Nitric Oxide, of Nitrogen in Nitrates and Nitrites.

1 c.c. NO at N.T.P.	= 0·6257	mgm.	N
,,	= 1·3402	,,	NO
,,	= 1·6975	,,	N_2O_3
,,	= 2·4121	,,	N_2O_5
,,	= 4·5176	,,	KNO_3
,,	= 3·7986	,,	$NaNO_3$
,,	= 2·8144	,,	HNO_3

* *Zeit. f. anal. Chem.* 1894, 33, 113. † *Analyst*, 1910, 307.

The two following methods give the nitrogen existing as both nitrate and nitrite in the substances analysed.

(i.) The Crum method. This method was described by W. Crum as far back as 1847. Originally devised for the analysis of nitrates and of gun-cotton, it was, in an improved form, used by Frankland and Armstrong for the determination of nitrates in water, for which purpose it is still largely used (see Water Analysis section).

(ii.) Lunge's nitrometer method. This is fully described in the section on technical gas analysis. It is used for the analysis of nitrous vitriol in sulphuric acid manufacture and for several other purposes.

NITRITES.

1. Iodimetric Method.

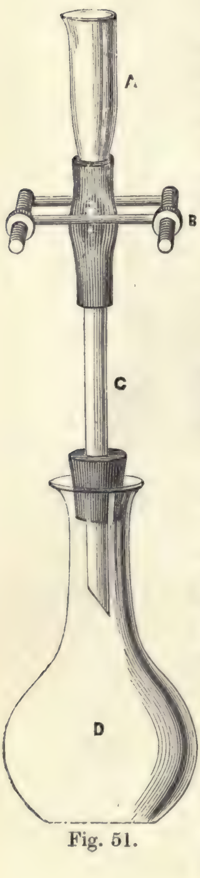


Fig. 51.

Dunstan and Dymond* have devised a method for the determination of N_2O_3 in organic and inorganic combination which is both simple in operation and accurate in results. The authors point out that although the inorganic nitrites may be accurately analysed by gasometric methods, or by permanganate, it is impossible to use such methods for the organic compounds or their alcoholic solutions. The reaction upon which the method depends is not new, being based on the following equation—

$$2HI + 2HNO_2 = 2H_2O + 2NO + I_2.$$

The liberated iodine is titrated with $^N/_{10}$ thiosulphate in the usual way. The chief merit in the process is the simple form of apparatus used, which is shown in fig. 51.

A stout glass flask, having a capacity of about 100 c.c., is closed by a tightly fitting rubber stopper, through which passes a piece of rather wide glass tubing (C), one end of which (that within the flask) is cut off obliquely, so that liquid may flow freely through it. The other end of the tube is connected by means of a piece of thick rubber tubing with a large glass tube, which forms a lipped funnel (A). A steel screw clamp (B) regulates communication between the funnel and the tube, and the short interval of rubber which is not occupied by glass tubing forms a hinge upon which the flask may be moved into a position at right-angles to the funnel, in order to mix by agitation the liquids

* *Pharm. Journ.* [3] **19**, 741.

which are introduced into the apparatus. The absence of any leak in the apparatus is ascertained by boiling about 50 c.c. of water in the flask until steam has continuously issued from the funnel for some few minutes, when the screw clip is quickly closed and simultaneously the source of heat is removed. A little water is now placed in the funnel and the flask is cooled by immersion in water. On sharply inverting the flask the "click" of the water against the airless flask should be quite distinct. No water should be drawn from the funnel or from any of the joints into the flask, and no diminution in the intensity of the "click" should be observed after the apparatus has been standing, neither when the flask is inverted and the funnel empty should any bubbles of air pass through into the liquid. Having thus proved the absence of any leak in the apparatus, it is ready for use. The flask is now free from all but mere traces of oxygen. A conclusive proof of this is obtained by boiling in the flask a solution of potassium iodide, acidified with diluted sulphuric acid, and then, after the closed flask has been cooled, the funnel removed and its place taken by a smaller glass tube filled with air-free water, the apparatus is connected with a reservoir of pure nitric oxide. When the clamp is unscrewed nitric oxide is drawn into the flask, and should any oxygen be present nitrous acid will be produced, and consequently iodine will be set free. This experiment has often been made by the authors, who have failed to observe any but an insignificant trace of liberated iodine.

METHOD OF PROCEDURE : 5 c.c. of a 10 per cent. solution of potassium iodide, 5 c.c. of a 10 per cent. solution of sulphuric acid, and 40 c.c. of water are introduced into the flask, which is securely fitted with the cork carrying the funnel and tube. The screw clip being open, and a free passage left for the escape of steam, the liquid is boiled. After a few minutes, when any iodine which may have been liberated has been expelled, and the upper part of the flask is completely filled with steam, which is also freely issuing from the funnel, the clip is tightly closed, and at the same moment the source of heat is removed. A little water is now put into the funnel, and also on the rim of the flask, as a safeguard against a possible minute leakage, and the vessel is cooled, by immersion in water. A solution containing a known weight of the nitrite (equivalent to about 0·1 gm. of nitrous acid) is placed in the funnel, and slowly drawn into the flask by cautiously unscrewing the clip. The liquid which adheres to the funnel is washed into the flask with recently boiled and air-free water, care being taken that during this operation no air is admitted into the flask. When experiments are being made with organic nitrites which are insoluble in water, they are dissolved in alcohol, and alcohol is also used to wash the funnel. When the nitrite is very volatile, a little cold alcohol should be put in the funnel, and the point of the pipette containing the nitrite should be held at the bottom of the funnel beneath the alcohol, and the liquid quickly drawn from the pipette into the flask. The nitrite having been introduced, the flask is well shaken and the liberated iodine is titrated with a standard solution of thiosulphate, small quantities of which are delivered from a burette into the funnel and gradually drawn into the flask ; the screw clip renders it quite easy to admit minute quantities of the solution. As soon as the iodine is decolorized any standard solution remaining in the funnel is returned to the burette. Or the funnel may, before the titration is commenced, be replaced by the burette itself, and the standard solution delivered direct into the flask. Starch may be used as an indicator, but it is usually quite easy to observe the complete disappearance of the yellow colour of the dissolved iodine. From the volume of the standard

solution used, the amount of nitrous acid is calculated from the equation befoie given.

It is obvious that the apparatus might be improved in several respects, as for example, by constructing it entirely of glass, with a ground stopper and tap, as well as by the use of a graduated funnel to deliver the standard solution, and also in other ways.

The authors quote numerous experiments, comparing the method with careful determinations of sodium and ethyl nitrites gasometrically, showing excellent results.

As a further test of the accuracy of the process, experiments were made with various organic nitrites of known purity. In each instance a solution of the nitrite was made by weight, and a weighed quantity was used for the determination. To prevent any loss of these volatile nitrites the experiments were conducted in the following manner :—A well-stoppered bottle half filled with the alcohol corresponding to the nitrite* to be determined was weighed. Enough of the nitrite was now introduced by means of a pipette to constitute approximately a 2 per cent solution, and the liquid again weighed. The exact strength of the solution having been thus determined, the contents of the bottle were well mixed, and the neck and stopper of the bottle dried. The bottle was now re-weighed, and about 2 c.c. of the solution removed by a pipette, care being taken not to wet the neck of the bottle. The liquid having been introduced into the flask without exposure to air, in the manner which has been previously described, the bottle containing the solution was again weighed. The results obtained with ethyl nitrite were :—

Taken.	Found.
0·088 gm.	0·089 gm.
0·176 ,,	0·179 ,,
0·113 ,,	0·115 ,,

2. Analysis of Alkali Nitrites by Permanganate.

Kinnicutt and Nef have devised the following method, and it gives good results if carefully managed.

The sample of nitrite is dissolved in cold water in the proportion of about 1 to 300 : to this liquid $^{N}/_{10}$ permanganate is added, drop by drop, till it has a permanent red colour ; then 2 or 3 drops of dilute H_2SO_4, and immediately afterwards a known excess of the permanganate. The liquid, which should now be of a dark red colour, is strongly acidified with pure H_2SO_4, heated to boiling, and the excess of permanganate determined by means of freshly prepared $^{N}/_{10}$ oxalic acid. 1 c.c. permanganate = 0·00345 gm. $NaNO_2$, or 0·00425 gm. KNO_2.

Of course, there must be no reducing substance other than the nitrite present in the material examined, and, to ensure accuracy,

* The corresponding alcohol was employed to prevent loss consequent on the occurrence of a reverse chemical change, which takes place when a lower homologous alcohol is mixed with the nitrite corresponding to a higher homologous alcohol; for example, a solution of amyl nitrite in ethyl alcohol soon becomes a solution of ethyl nitrite in amyl alcohol, from which the ethyl nitrite rapidly volatilizes

a blank experiment should be made with the like proportions of H_2SO_4 and oxalic acid.

3. Gasometric Method.

P. Frankland* adopts this method for the determination of nitrous acid in small quantity, but too large for colorimetric determination, and where also ammonia, organic matters, and nitrates may co-exist. It is based on the fact that when nitrous acid, together with excess of urea, is mixed with sulphuric acid in the cold, the reaction is

$$CO(NH_2)_2 + 2HNO_2 = 2N_2 + CO_2 + 3H_2O.$$

The decomposition is made in the Crum-Frankland shaking tube, described and figured in Part VI., and the evolved nitrogen gas measured in the usual gas apparatus. The ordinary nitrometer may also be used for large quantities of NO by the same method.

In the case of an ordinary alkali nitrite, the dry substance, or its solution evaporated to dryness, is mixed with excess of crystallized urea, and dissolved in about 2 c.c. of boiling water in a beaker, then transferred, with the rinsings, to the cup of the apparatus, and passed into the tube. A few c.c. of dilute sulphuric acid (1 : 5) are then passed in. A vigorous evolution of gas takes place, and continues for some five minutes; the gas is a mixture of nitrogen and carbonic anhydride. The decomposition is complete in fifteen minutes. A solution of pure sodium hydrate (1 : 3) is now added through the cup, and the mixture violently shaken, until the CO_2 is absorbed. The gas and liquid are then transferred, by means of another mercury trough, to the laboratory vessel, and the gas, which is double the volume of the N existing as N_2O_3, measured in a gas apparatus, and its weight calculated in the usual way.

EXAMPLE: A solution of sodium nitrite was made and standardized with permanganate, the result being that 10 c.c. =0·01346 gm. N. 10 c.c. of the same solution were evaporated to dryness in a small beaker, about 0·2 gm. of urea added, the whole dissolved in 2 c.c. of hot water, which, with the rinsings, were transferred through the cup into the tube, treated with sulphuric acid and caustic soda, then transferred to the gas apparatus with the following results:—Volume of N, 13·8 c.c.; mercurial pressure, 127·5 mm.; temperature, 17·7° C. The weight of N thus found, after the necessary corrections, was 0·01346 gm.

The Crum-Frankland mercury method, described in the section on Water Analysis, and in which the same shaking tube is used, does not distinguish between nitric and nitrous nitrogen; but P. Frankland required a method for the determination of nitrous acid in a mixture of nitrates, peptones, sugar, and various salts occurring in a solution used for cultivation of micro-organisms. The experiments carried out by him showed that when such a mixture was evaporated to dryness the loss of HNO_2 was considerable, and the results came out much too low. Further experiment, however, showed that the addition of a slight excess of caustic

* *J. C. S.* **53**, 364.

potash during evaporation prevented the loss of any HNO_2; and on the other hand the addition of a slight excess of ammonium chloride entirely destroyed it. Therefore by a combination of the mercury and the urea methods, the determination of nitric and nitrous acids may be satisfactorily accomplished, the destruction of the HNO_2 on the one hand being effected by excess of NH_4Cl, whilst on the other hand all loss of HNO_2 may be avoided by evaporation with caustic alkali. The mode of procedure has the advantage over all differential methods in that each acid is determined individually and independently of the other.

4. Mixtures of Nitrites with Alkali Sulphites and Thiosulphates.

Lunge and Smith* have shown that the only satisfactory method of completely oxidizing sulphites and thiosulphates by permanganate is to add to the solution a large excess of permanganate, more than sufficient for complete oxidation, and accompanied with formation of MnO_2. Excess of $FeSO_4$ is then added, and again permanganate till pink. When such a mixture contains nitrites, they will of course be oxidized to nitrates.

To find the amount of nitrites present, therefore, the following plan is adopted :—

METHOD OF PROCEDURE : The solution of the substance in not too large quantity is oxidized exactly as described, a known volume of standard ferrous sulphate is added, together with a large excess of strong H_2SO_4. The mixture is boiled nearly to dryness in a flask with slit valve, diluted, and, when cool, titrated with permanganate. The difference between the volume then required and that required by the original $FeSO_4$, represents the nitric acid which has been reduced and escaped as NO.

The exceedingly delicate colorimetric method of determining nitrites originally devised by Griess, and improved by others, will be described in the section on Water Analysis.

DISSOLVED OXYGEN.

$O=16.$

THE volumetric determination of the dissolved oxygen in water is an operation of some importance in water analysis. It is well known that organic and bacterial contamination generally exist side by side; the organic matter offering suitable pabulum for the growth of bacterial life. Water thus contaminated is de-oxygenated by the living organisms which consume oxygen during their growth; hence the importance of the determination of dissolved oxygen in water, as a means of ascertaining the co-existence of the two kinds of impurity.

In brewing also a knowledge of the state of aeration of the wort is sometimes of importance, especially at the fermentation stage of the process.

Several methods have been proposed for carrying out the

* *J. S. C. I.* 2, 465.

determination. Mohr's method, depending on the exidation of ferrous compounds, with subsequent titration by permanganate, has not come greatly into use. Winkler* proposed to take advantage of the oxidation of manganous hydroxide (obtained by mixing solutions of a manganous salt and caustic alkali) by dissolved oxygen, the higher oxide formed being decomposed by sulphuric acid and potassium iodide with liberation of iodine, which is determined by titration with sodium thiosulphate. This method is interfered with by the presence of nitrites, which also liberate iodine from acidified potassium iodide ; great organic contamination also interferes, inasmuch as the impurities present take up a portion of the liberated iodine.

Schützenberger's method,† fully described in the sixth edition of this book, has received great attention from many operators, some of whom have reported favourably, whilst others find the process unreliable. The reason for the anomalies apparent in the reports of the various experimenters is shown in the results of an interesting and critical investigation of the process carried out by Roscoe and Lunt,‡ They show that an important disturbing influence had been overlooked, and explain many previously ill-understood points in the process.

Schützenberger's original process depends on the reducing action of sodium hyposulphite Na_2SO_2, prepared by the action of zinc dust on a saturated solution of sodium bisulphite containing an excess of sulphurous acid. The determination was originally carried out in a large Woullfe's bottle, of about two litres capacity, filled with pure hydrogen. About 20–30 c.c. of water were introduced and slightly coloured blue by indigo-carmine solution. The blue colour was then cautiously discharged by the careful dropping in of hyposulphite solution. To the yellow reduced liquid thus produced, the water to be examined was added from a pear-shaped vessel holding about 250 c.c. The dissolved oxygen restored the blue colour by oxidation, and the amount of hyposulphite required again to decolorize the liquid was noted.

Schützenberger showed that when a small amount of indigo was employed in the determination, the yellow colour produced when the titration was completed quickly returned to blue, and this when decolorized again turned blue, and so on for some time, until double the amount of hyposulphite first added had been used. He showed also that by using a much larger amount of indigo the double portion of hyposulphite was required *at once*.

By titrating an ammoniacal solution of copper sulphate with the hyposulphite used he arrived at a value (though an erroneous one) for the hyposulphite employed in his experiments, and concluded that, at the first yellow colour produced in a titration where a small amount of indigo was used, only *half* the oxygen actually present

* *Berichte*, 1888, 2851.

† See "Fermentation" by P. Schützenberger (*International Scientific Series*).

‡ *J. C. S.* 1889, 552.

had been obtained. The other half he accounted for by saying that the reaction between hyposulphite and dissolved oxygen is such that one-half the oxygen becomes latent as hydrogen peroxide, which slowly gives up half its oxygen. He thus accounted for the return of the blue colour, as well as his observation that only half the oxygen was at once obtained. To explain the observation that when a large amount of indigo was employed *the whole* of the dissolved oxygen was found, he assumed that a different reaction takes place, one between dissolved oxygen and reduced indigo, in which the peroxide of hydrogen is not formed.

Ramsay and Williams,* whilst agreeing with Schützenberger and with Dupré,† that the process gives reliable results, throw a doubt on the chemical explanation given of the above experiments.

Instead of the ratio 1 : 2, they find 3 : 5 to be the ratio between the first and the total quantity of hyposulphite required when a small amount of indigo is employed, but give it only as the mean expression of the varying ratios they obtain, and add " but it is difficult to devise an equation which will in a rational manner account for this partition of oxygen " into two stages of the process. Roscoe and Lunt's investigation‡ has thrown a new light on these experiments. They show (1) that a series of fifteen determinations carried out with every care in improved apparatus, and under apparently identical conditions, gave discordant results, varying between 4·55 and 6·50 c.c. of hyposulphite for the same volume of water, showing a difference of 0·35 per cent. of the mean value. (2) The rapidity of titration has a great influence on the result. The mean of a series of ten determinations carried out drop by drop was 5·47, whilst ten experiments with the same sample of water gave a mean of 7·12 when the titration was performed quickly. (3) Not only is a low result obtained by a slow titration and a high result by a quick one, but by varying the time of titration still more, *extreme* variations in the result are obtained; any value between 1 and 100 per cent. of the total oxygen present being shown to be possible. (4) The ratio between the first reading and the total quantity of hyposulphite required is not a constant one, and is shown to be capable of an infinite range of variation.

The key to the explanation of these remarkable results is given by the authors as follows :—" The conclusion " from their experiments " was, that when aerated water is introduced into an atmosphere of pure hydrogen, it immediately begins to lose oxygen by *diffusion* into the hydrogen until an equilibrium is established." By the recognition of this disturbing influence, the previous anomalies are easily explainable on the following data.

(1) Discordant results are obtained from the same water, because the several titrations are not performed in exactly the same time, therefore, varying amounts of oxygen diffuse, and leave a varying residue for titration.

* *J. C. S.* 1886, 751. † *Analyst* 10, 156. ‡ *J. C. S.* 1889, 552.

(2) The high results of a quick titration are accounted for by the fact that a large amount of oxygen is titrated *and fixed* before it has had time to diffuse, whilst the slow titration gives a low result, because a large amount of oxygen has already diffused from the liquid before the titration is completed. No greater proof of the

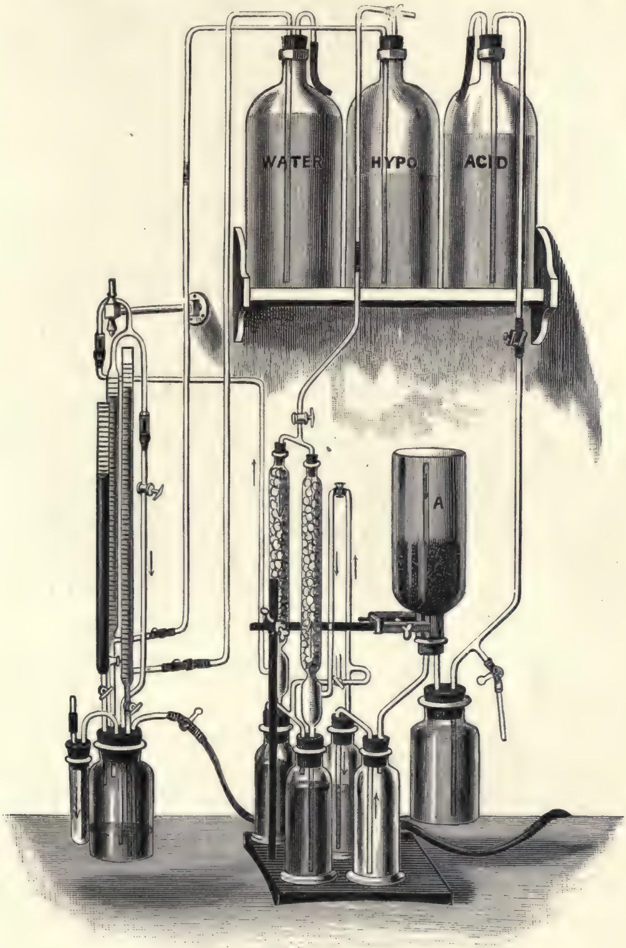


Fig. 52.

rapidity with which the water under examination lost oxygen by the old process need be given than the fact that Schützenberger's results show that half the oxygen had left the liquid by diffusion before the determination could be completed.

(3) The return of the blue colour is due to the re-absorption of the *diffused* oxygen by the sensitive yellow liquid, oxidation by

gaseous oxygen producing the blue colour, which is thus not due to a reaction within the liquid.

(4) The whole of the oxygen is obtained when a large amount of indigo is used, because when reduced it is capable of *at once* fixing the whole of the dissolved oxygen and thus prevents diffusion. The use of so large a quantity of indigo, necessary to effect this result, however, so disturbs the end-reaction that "it is difficult to fix the point at which the last trace of blue has been discharged with any degree of accuracy" (Dupré *loc cit.*). Hence a new method must be resorted to in which diffusion is eliminated, and Roscoe and Lunt have devised the following method to satisfy the conditions of the case. The apparatus employed by them is shown in fig. 52.

It consists essentially of (1) an apparatus for the continuous generation and purification of hydrogen, by the action of dilute sulphuric acid on zinc; (2) a 200 c.c. wide-mouthed bottle, fitted with three burettes with glass taps, inlet and outlet tubes for a current of hydrogen, and an outlet tube for the titrated liquid; (3) Winchester stock bottles of hyposulphite, indigo (not shown), and water (sample), communicating with their respective burettes by *glass** siphons. The hydrogen generated in A passes through two wash-bottles containing caustic potash, thence through two Emmerling's tubes filled with glass beads, moistened with an alkaline solution of potassium pyrogallate, an arrangement being made whereby the beads may be re-moistened with fresh pyrogallate from the bottles beneath, the liquid being forced up by hydrogen pressure. Pure hydrogen is supplied continuously (1) to the stock bottle of hyposulphite, (2) to the hyposulphite burette, and (3) to the titration bottle.

Preparation of the Reagents.—The reagents required are—
Hyposulphite solution.
Indigo solution.
Standard aerated distilled water.

The Hyposulphite solution is prepared by dissolving 125 gm. of sodium bisulphite in 250 c.c. of water, and passing a current of SO_2 through the solution until saturation is effected. The solution is poured into a stoppered bottle of about 500 c.c. capacity, containing 50 gm. of zinc dust, the bottle is almost filled up with water, and the mixture well shaken for five minutes, after which the bottle is placed beneath a running tap to cool. The mixture is again agitated after a quarter of an hour and left to deposit the excess of zinc. The clear liquid is poured off from the sediment into a Winchester quart bottle half full of water. Milk of lime is added in excess, and the solution made up to fill the bottle almost

* India-rubber tubing must not be used for the conveyance of the hyposulphite solution (or the water under examination), as atmospheric oxygen rapidly diffuses through the india-rubber and affects the strength of the solution.

completely. The mixture is now thoroughly shaken and allowed to stand (best overnight) until clear.

The solution thus obtained is much too strong for use. 200 c.c. of this may be poured into a Winchester quart bottle of water (never into a bottle filled with air) and well shaken with as little air as possible. The approximate strength of this dilute solution must now be found by titrating good tap water in the apparatus already described. The strength should be such that 100 c.c. of water requires about 5 c.c. of hyposulphite, and the solution should be made up approximately to this value. It slowly loses strength on keeping, even in hydrogen, and its value should be determined daily as required to be used.

The Indigo-carmine solution is really sodium or potassium sulphindigotate, and is prepared by shaking up 200 gm. of this substance in a Winchester quart bottle of water, and filtering the blue solution, which must be diluted to such a strength that 20 c.c. require about 5 c.c. of the above hyposulphite solution for decolorization.

Standard Aerated Distilled Water—Two Winchester quart bottles half filled with freshly distilled water are vigorously agitated for five minutes, and the air renewed several times by filling up one bottle with the contents of the other, and again dividing into two portions, which are repeatedly shaken with fresh air. Finally, one bottle being filled, the temperature of the water is taken, and also the barometric pressure, after which the bottle is allowed to stand stoppered for half an hour, to get rid of minute air-bubbles. Table No. 8, due to Roscoe and Lunt, gives the volume of oxygen contained in this standard aerated water, and the results show that Bunsen's co-efficients, previously used, are inaccurate.

THE DETERMINATION : The burette having been filled, and a preliminary trial made—

(1) 20 c.c. of the water are introduced into the small bottle and about 3 c.c. of indigo solution added.

(2) A moderate current of hydrogen is passed through the blue liquid by a very fine jet for three minutes to free both water and supernatant gas from free oxygen.

(3) Hyposulphite is now carefully added, during the flow of hydrogen, until the change from blue to yellow occurs, taking care not to overstep this point.

(4) A further measured quantity of hyposulphite is now added (say 10 c.c.) sufficient to combine with all the dissolved oxygen in the volume of water (50–100 c.c.) proposed to be used in the determination.

(5) The important point is that the water be now quickly run in from a burette by a capillary tube passing *beneath the surface of the liquid* to the bottom of the vessel. The water is thus introduced into a liquid which will *at once* fix the free oxygen and thus prevent its diffusion on coming in contact with the hydrogen, the reduced indigo acting as an indicator for the complete oxidation of the hyposulphite. The liquid is kept in constant motion during the addition of the water, which is shut off the moment a permanent blue colour appears.

(6) The blue is decolorized by a further slight addition of hyposulphite. The

volume of water used and the total hyposulphite, minus the first addition, are noted and the determination repeated for confirmation.

When the water contains very little oxygen the second addition of hyposulphite may be omitted, the reduced indigo being sufficient to take up all the dissolved oxygen. In this case, care must be taken that the oxygen added should require not more than half the hyposulphite first added to decolorize the indigo.

Standardizing the Hyposulphite.—In order to complete the determination it is necessary to know the strength of the hyposulphite solution employed, and for this purpose the bottle of standard aerated distilled water is titrated. This method has the great advantage that it is a titration carried out under almost the same conditions as the examination of the sample. The result of a determination is easily obtained by the following formula :—

$$\frac{d \times hs \times Od}{s \times hd} = x \text{ c.c. dissolved Oxygen per litre of water}$$

where d and s = the volumes of distilled water and sample respectively used, hd and hs = the hyposulphite required for the distilled water and sample respectively, and Od the volume of dissolved oxygen contained in one litre of the standard water.

Standardizing the Indigo.—When once the hyposulphite has been carefully standardized by distilled water, the rather troublesome aeration may be avoided by finding the oxygen value of the indigo solution. This solution remaining constant may be used for the subsequent standardizing of the hyposulphite.

It is only necessary to take a suitable quantity of indigo solution, diluted with water if necessary, free it from all dissolved oxygen by a current of pure hydrogen continued for five minutes, then carefully decolorize with hyposulphite, the value of which has been found by using aerated distilled water.

The authors show that Schützenberger's method of standardization, depending on the decolorization of ammoniacal copper sulphate, gives inaccurate results.

Free acids or alkalies greatly disturb the process. Bicarbonates have no effect. Of course when substances other than oxygen, which decompose hyposulphite, are present, the accuracy of the method is proportionately disturbed. The authors have applied the process to waters of very varied character, and containing widely different amounts of oxygen, and show that the method is capable of giving good results, compared with the actual volume of oxygen found by extracting the gases by boiling *in vacuô*.

The delicacy of the reaction is such that one part of oxygen in *two million* parts of water is easily detected.

The following numbers were obtained from five different samples of London tap water collected on five different days.

	(1)	(2)	(3)	(4)	(5)
	c.c.	c.c.	c.c.	c.c.	c.c.
Nitrogen	13·22	13·95	13·36	13·43	13·49
Oxygen	5·15	5·91	5·38	6·31	5·80
Carbon dioxide	7·98	9·29	6·70	7·35	8·11
Total Gas	26·35	29·15	25·44	27·09	27·40
Oxygen by the new volumetric method	5·52	6·13	5·64	6·41	6·24
Gas obtained	5·15	5·91	5·38	6·31	5·80
Difference	0·37	0·22	0·26	0·10	0·44
Mean difference 0·28 c.c. oxygen per litre of water.					

The oxygen values obtained by the two methods show close agreement, considering the possible experimental error in so complex a comparison.

M. A. Adams* describes and figures a very convenient arrangement for carrying out this process, which is well adapted for technical work, and less cumbrous than the apparatus here described.

Iodimetric Method.

A simpler method than the foregoing has been proposed by Thresh,† which by comparison with Roscoe and Lunt's method appears to give satisfactory results when aerated distilled water was under titration, the differences occurring only in the second decimal place. The author was led to investigate the method by observing the larger amount of iodine which a very minute quantity of a nitrite caused to be liberated when potassium iodide and dilute sulphuric acid were added to water containing it. The amount of iodine liberated varies with the length of exposure to air. If air is excluded no increase of free iodine occurs after the first few minutes, and if the water is previously boiled and cooled in an air-free space still less iodine is liberated. In this latter case the action is represented by the equation—

$$2HI + 2HNO_2 = I_2 + 2H_2O + 2NO.$$

When oxygen has access to the solution, the nitric oxide acts as a carrier, and more hydrogen iodide is decomposed, the nitric oxide apparently remaining unaffected, and capable of causing the decomposition of an unlimited quantity of the iodide.

This reaction is the one utilized in the process devised by Thresh

* *J. C. S.* **61**, 310. † *J. C. S.* **57**, 185.

for determining the oxygen dissolved in water. As 16 parts by weight of oxygen will liberate 253·84 parts of iodine, thus—

$$2HI + O = H_2O + I_2,$$

and as the latter element admits of being accurately determined, theoretically the oxygen should be capable of very precise determination. Practically such is the case; the oxygen dissolved in drinking waters admits of being determined both rapidly and with precision. It is only necessary to add to a known volume of the water a known quantity of sodium nitrite, together with excess of potassium iodide and acid, avoiding access of air, and then to determine volumetrically the amount of iodine liberated. After deducting the proportion due to the nitrite used, the remainder represents the oxygen which was dissolved in the water and in the volumetric solution used.

The following are the reagents required :—

(1) Solution of sodium nitrite and potassium iodide :—

Sodium nitrite	0·5 gm.
Potassium iodide	20·0 gm.
Distilled water	100 c.c.

(2) Dilute sulphuric acid :—

Pure sulphuric acid	1 volume
Distilled water	3 volumes

(3) A clear, freshly made solution of starch.

(4) A volumetric solution of sodium thiosulphate :—
Pure crystals of thiosulphate, 7·75 gm.
Distilled water to 1 litre.
1 c.c. corresponds to 0·25 milligram of oxygen.

The apparatus required is very simple, and can readily be fitted up. It consists of a wide-mouthed white glass bottle (A, fig. 53) of about 500 c.c. capacity, closed with a caoutchouc stopper having four perforations. Through one passes the tube B, drawn out at its lower extremity to a rather fine point, and connected at the upper end, by means of a few inches of rubber tubing, with the burette C, containing the thiosulphate. Through another opening passes the nozzle of a separatory tube D, having a stopper and stopcock. The capacity of this tube when full to the stopper must be accurately determined. Through the third opening passes a tube E, which can be attached to an ordinary gas supply. Through the last aperature is passed another tube, for the gas exit, and to this is attached a sufficient length of rubber tubing to enable the cork G at its end to be placed in the neck of the tube D when the stopper is removed. A small piece of glass tube projects through the cork, to allow of the escaping gas being ignited.

The apparatus is used in the following manner :—The bottle A

being clean and dry, the perforated bung is inserted, the burette charged, and the tube B fixed in its place. E is connected with the gas supply. The tube D is filled to the level of the stopper with the water to be examined, 1 c.c. of the solution of sodium nitrite and potassium iodide added from a 1 c.c. pipette, then 1 c.c. of the dilute acid, and the stopper instantly fixed in its place, displacing a little of the water, and including no air. If the pipette be held in a vertical position with its tip just under the surface of the water, both the saline solution and the acid, being much denser than the water, flow in a sharply defined column to the lower part of the tube, so that an infinitesimally small quantity (if any) is lost in the water which overflows when the stopper is inserted. The tube is next turned upside down for a few seconds for uniform admixture to take place, and then the nozzle is pushed through the bung of the bottle, and the whole allowed to remain at rest for 15 minutes, to enable the reaction to become complete. A

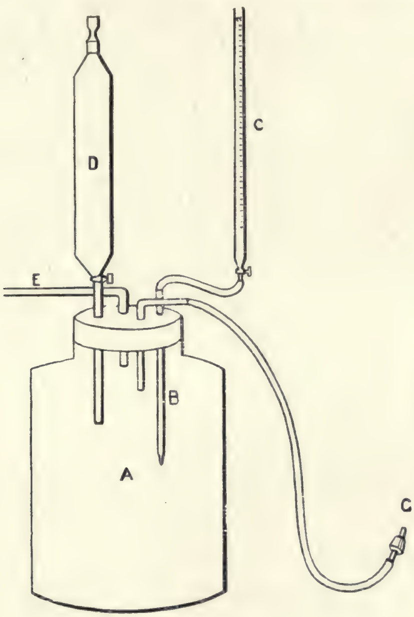


Fig. 53.

rapid current of coal gas is now passed through the bottle A, until all the air is displaced and the gas burns at G with a full luminous flame; the flame is now extinguished, the stopper of D removed, and the cork G rapidly inserted. On turning the stopcock, the water flows into the bottle A. The stopcock is turned off, the cork G removed, and the supply of gas so regulated that a small flame only is produced when this gas is ignited at G. Thiosulphate is

now run in until the colour of the iodine is nearly discharged. A little starch solution is then poured into D, and about 1 c.c. allowed to flow into the bottle by turning the stopcock. The titration with thiosulphate is then completed. After the discharge of the blue colour, the latter returns faintly in the course of a few seconds, due to the oxygen dissolved in the volumetric solution ; after standing about two minutes, from 0·05 to 0·1 c.c. of thiosulphate must be added to effect the final discharge. The amount of volumetric solution used must now be noted. This will represent a, the oxygen dissolved in the water examined, $+b$, the nitrite in the 1 c.c. of solution used, and the oxygen in the acid and starch solution $+c$, a portion of the dissolved oxygen in the volumetric solution. To find the value of a, it is obvious that b and c must be ascertained. This can be effected in many ways, and once known does not require re-determination unless the conditions are changed.

To find the value of b.—Probably the best plan is to complete a determination as above described, and then, by means of the stoppered tube, introduce into the bottle in succession 5 c.c. of nitrite solution, dilute acid, and starch solution. After standing a few minutes, titrate. One-fifth of the thiosulphate used will be the value required.

To Find the Value of c.—This correction is a comparatively small one, and admits of determination with sufficient accuracy if it is assumed that the thiosulphate solution normally contains as much dissolved oxygen as distilled water saturated at the same temperature. Complete a determination as above described, then remove the stoppered tube, and insert a tube similar to that attached to the burette, and drop in from it 10 or 20 c.c. of saturated distilled water exactly as the thiosulphate is dropped in. Allow to stand a few minutes and titrate. One-tenth or one-twentieth of the volumetric solution used, according to the number of c.c. of water added, will represent the correction for each c.c. of volumetric solution used. Call this value d.

Let e be the number of c.c. of thiosulphate used in an actual determination of the amount of oxygen in a sample of water ;

f = the capacity in c.c. of the tube employed -2 c.c., the volume of reagents added ;

g = the amount of oxygen in milligrams dissolved in 1 litre of the water ;

then
$$g=\frac{1000}{4f}(e-b-ed).$$

With a tube made to hold exactly 250 c.c., the most convenient quantity to use, $\frac{1000}{4f}$ becomes unity, and

$$g=e-b-ed.$$

In the author's experiments two nitrite solutions were used ; in the first $b=2·1$ c.c., in the second 3·1 c.c. A number of determinations

of d were made, at temperatures varying from 40° to 60° F. The value of d was found to vary between 0·03 and 0·0315. In all the author's recent experiments d was taken as 0·031.

When $e=3$ c.c. the reaction seems to be complete in five minutes, but, to be on the safe side, it is better to fix the minimum at fifteen minutes.

The use of coal-gas is recommended by the author without passing it over alkaline pyrogallol or otherwise treating it before allowing it to pass through the apparatus.

The results obtained, however, can be made to vary, the extreme limit being less than 0·5 milligram of oxygen per litre of water, using 250 c.c. for the determination. To quote an extreme case. In one experiment (1), after the air has been wholly expelled from the bottle A, no more gas was passed through, and the titration was effected in the closed apparatus, the volumetric solution being run in as rapidly as possible. The end-reaction was not well defined. In the second experiment (2), the volumetric solution was run in very slowly drop by drop, and a brisk current of gas was kept passing through the apparatus. End-reaction well defined.

	Volume of water.	Thiosulphate.	Oxygen per litre.
(1)	322 c.c.	15·35 c.c.	9·14 milligrams.
(2)	322 ,,	14·9 ,,	8·80 ,,

The difference is probably due to nearly all the oxygen dissolved in thiosulphate being used up in the first case, and being lost by diffusion in the second.

In the examination of waters from various sources, and making the experiments in pairs, using tubes of different sizes, the author found that exceedingly concordant results could easily be obtained.

In determining the oxygen in distilled water saturated with air, the author found that the results at 25° and 30° C. were higher than those obtained by Roscoe and Lunt, whilst at the lower temperatures they were almost identical, and it occurred to him that the difference was probably due to the mode of saturation. The agitation in a couple of Winchesters was done as directed by them, but the water used had been previously saturated at the lower temperatures, and probably were slightly super-saturated. A further series of experiments were then made with freshly-distilled water, which was not agitated with air until it had attained the desired temperature. The results proved that this surmise was correct. Probably some such explanation accounts for the uniformly higher results obtained by Dittmar.

No doubt there will be exceptional cases in which the process cannot be used, and others in which some modification may be required. A water containing nitrites will require the amount of the nitrous acid to be determined if the utmost accuracy is required. (A water containing one part of HNO_2 in 1,000,000, will affect the results $+0·17$ milligram of oxygen per litre, 94 parts of the acid

corresponding to 16 of oxygen.) Where nitrites are present in sufficient quantity to interfere, the amount may be determined by any of the ordinary processes, but the author prefers the following method :—

To 250 c.c. of the water to be examined, rendered faintly alkaline if not already so, add a few drops of strong solution of potassium iodide, and boil vigorously for a few minutes. Then transfer to the bottle A used in the oxygen determination, and allow to get quite cold in a slow current of coal gas. Then add a few drops of dilute sulphuric acid and solution of starch, and titrate with the thiosulphate. The correction to be made in the oxygen determination is thus ascertained. One or two experimental results may be quoted.

		Quantity of water.	Thiosulphate used.	Corrected.	Milligrams of oxygen per litre.
1..	Tap water	232·5	13·2	9·7	10·43
2	Tap water + 5 milligrams commercial sodium nitrite	232·5	15·95	9·55	10·27
3	Tap water + 10 milligrams sodium nitrite	232·5	18·6	9·48	10·19

In number 2, the thiosulphate used by 250 c.c. of the boiled water was 2·8 c.c.

In number 3, the thiosulphate used by 250 c.c. of the boiled water was 5·45 c.c.

The results are fairly satisfactory, even with such large proportions of nitrite, proportions far larger than are likely to be met with in practice.

Nitrates do not interfere, even when present in large quantities ; but fresh urine, when present to the extent of 1 per cent., has a small but very appreciable effect.

The following is an example of the method at ordinary temperature :—

Temperature 15° *C.*

	Quantity of water taken.	Thiosulphate used.	*c—b—ed.*	Milligrams of Oxygen per litre.	Difference from mean.
1..	322·0	15·45	12·87	9·99	−0·04
2..	322·0	15·55	12·97	10·07	+0·04
3..	232·5	11·90	9·43	10·14	+0·11
4..	232·5	11·70	9·23	9·92	−0·11
			Mean	10·03	

Barometer reading 760 mm.

10·03 milligrams = 7·02 c.c. at N.P.T.

Roscoe and Lunt found 6·96 „ Difference + 0·06.

Determination of the dissolved Oxygen in Waters and Effluents by Winkler's Method as modified by Rideal and Stewart.*

The principle on which this method depends is the oxidation in an alkaline liquid of manganous oxide to a higher oxide of manganese, the subsequent liberation of iodine from potassium iodide by this in the acidified solution, and the titration of the liberated iodine by thiosulphate.

The following solutions are required :—

1. Decinormal permanganate of potash.
2. A 2 % solution of potassium oxalate.
3. A 33 % solution of manganous chloride.
4. A mixed solution containing 50 % caustic soda and 10 % potassium iodide.†
5. $^{N}/_{20}$ sodium thiosulphate (1 c.c. = 0·006346 gm. iodine = 0·0004 gm. oxygen).

METHOD OF PROCEDURE: The temperature having been noted, a stoppered bottle of known capacity (300-350 c.c. when full) is completely filled with the sample of water or effluent (filtered or unfiltered, as may have been decided), avoiding any appreciable aeration in doing this, and 1 c.c. sulphuric acid is added, together with enough of the permanganate solution to leave a slight pink colour after the whole has been mixed and has stood for 10 minutes—the object being to oxidize any nitrite present to nitrate. If more than 10 c.c. of decinormal permanganate are required for this purpose, 2 c.c. of acid must be added instead of 1 c.c. The proper amount of permanganate to be added is best determined by a preliminary trial on 50 c.c. of the original liquid; this having been done, the amount required for the bottle-full is calculated and about 0·1 c.c. in excess of the calculated amount is added. The contents of the bottle are mixed by rotation and allowed to stand 10 minutes, after which any excess of permanganate is destroyed by the addition of 0·5 to 1·0 c.c. of the oxalate solution by means of a pipette, the neck filled up with the sample under examination, the stopper inserted, and the bottle rotated as before. The colour quickly disappears, and when decolorized 1 c.c. of the manganous chloride is passed to the bottom of the liquid from a long pipette, and immediately afterwards 3·0 c.c. of the mixed soda and iodide solution in the same manner. The stopper is inserted without air bubbles and the contents mixed by inversion and rotation. The liberated manganous hydroxide absorbs the free oxygen. On standing a few minutes the precipitated oxides of manganese settle; the stopper is then removed for a second and 3 c.c. of pure concentrated HCl (free from chlorine) are passed to the bottom by a pipette. The bottle is then closed and again rotated, and kept in the dark for 5 to 10 minutes, with frequent shaking, till clear. The liquid is then transferred to a porcelain dish and the iodine determined by thiosulphate and starch. The oxygen-equivalent of the latter being known, the amount of dissolved oxygen present in the sample is readily calculated. The reagents being used in the concentrated form with a comparatively large volume of water the correction for the additions is small and can usually be neglected. When, however, the oxygen is low, the reagents being presumably saturated with oxygen under atmospheric conditions, will make the result too high. The correction then to be applied is:

$$x = \frac{1000\,a - \mathrm{R}n}{\mathrm{V} - n}$$

* *The Analyst*, **26**, 1901, 141.

† Dr. Mc. Gowan has for a long time past (1910) used a solution of 700 gm. KOH and 100 gm. KI made up to 1 litre, about 4 c.c. being used in each determination.

Where x = no. of c.c. of oxygen at N. T. P. per litre of the liquid.
a = the amount of oxygen in c.c. found by titration.
V = the volume of the bottle.
n = the volume of the reagents.
R = no. of c.c. of oxygen contained in a litre of saturated water at the temperature of the experiment.

(R can be obtained from Roscoe and Lunt's table, or, preferably, is actually determined.)

Results have usually been given in c.c. of oxygen at N.T.P. per litre, with the temperature of the water; but in the Fifth Report of the Royal Commission on Sewage Disposal (see Water Section) the absorption of dissolved or atmospheric oxygen by an effluent is expressed in parts by weight per 100,000.

NOTE.—1 gram of oxygen occupies 699·79 c.c. at N.T.P.

Rideal and Burgess* have recently modified Winkler's process into a colorimetric method, which will give fair results even in the presence of nitrites, and is applicable to final sewage effluents in most cases.

METHOD OF PROCEDURE: A series of colour standards are first constructed corresponding to various proportions of oxygen from 0 to 1·5 parts per 100,000, proceeding by increments of 0·1 part as follows. Square-shouldered stoppered bottles of nearly colourless glass are carefully selected of a capacity of about 130 c.c. apiece when completely full—those actually selected not varying *inter se* by more than about 1·5 c.c. Into 15 of these bottles are run 90 c.c. of distilled water (free from organic matter), 1·5 c.c. of 10 % KI and 0·15 c.c. conc. HCl. The iodine tints can very easily be obtained by running into the series of bottles the calculated quantities of a standard solution of $K_2Mn_2O_8$ (0·395 gram per litre, same as used in water analysis). For example, a bottle holding 131·5 c.c. requires 13·15 c.c. of the solution to produce an iodine tint corresponding to 1 part of dissolved oxygen per 100,000. The bottles are then filled up with distilled water except for a minute bubble of air, the stoppers tightly inserted, and the contents mixed by agitation. The iodine standards should be kept in a closed box and comparisons should only be made in diffused light, the standards being put away immediately after use; in this way they may be relied on for over a month.

The water to be examined is siphoned with care into one of the test-bottles, 0·5 c.c. of nearly saturated $MnCl_2$ solution added, and then 1·5 c.c. of a solution containing 30 % NaOH and 10 % KI. The stopper is inserted, and the contents well mixed. After the oxidation of the manganous hydrate has taken place, and the precipitate has settled down somewhat, the stopper is withdrawn, and 1·5 c.c. conc. HCl added. The stopper is then reinserted, and the contents of the bottle well mixed. As the reaction with the acid causes a slight elevation of temperature and consequent expansion of the liquid, the stopper has a tendency to get loose, and it is convenient to plunge the test-bottle into a large basin of cold water and to turn it about until the stopper is tight again. After wiping the bottle, the tint of the liberated iodine is compared with the standards, and it is best to do this by holding the bottles in an inclined position a few inches above a white card and looking down through their shoulders. After a little practice there is no difficulty in estimating the fractions between the standards to within 0·03 part of oxygen. The results obtained compare well with the titrations by Winkler's method.

In this method, when a water contains nitrite, there is no trouble through NO acting as an oxygen-carrier, since the reaction of the nitrite, iodide, and acid takes place in a solution from which the free oxygen has already been removed

* *Analyst*, 1909, **34**, 193.

by the manganese hydrate. The iodine liberated on account of nitrite is consequently that of the ordinary equation—

$$2NaNO_2 + 2KI + 4HCl = 2NaCl + 2KCl + 2NO + I_2 + 2H_2O.$$

Hence, for two atoms of nitrous nitrogen we have to allow for one atom of oxygen; so that if a water contained 1·4 parts of nitrous nitrogen, the iodine liberated would be equivalent to 0·8 part of oxygen. Experiments have proved that when nitrites are determined and thus allowed for the colorimetric process still gives good results.

Effluents that are very turbid or have much dark-coloured suspended matter are best titrated.

The **rate of absorption** of dissolved oxygen by a sample of sewage or effluent affords a measure of the readiness with which it will deprive a stream of its dissolved oxygen when the two are mixed. Scudder* makes this determination as follows:—

100 c.c. of the sewage effluent are added to 900 c.c. of tap water in a half Winchester quart bottle, mixed by shaking, and allowed to stand for at least half an hour to allow small bubbles to rise to the surface. The dissolved oxygen in the diluted effluent is then determined. Two 10-oz. stoppered bottles are completely filled with the diluted effluent and placed in an incubator at a temperature of 75° Fah.† The dissolved oxygen is determined in one of these after the expiration of 24 hours, and in the other after 48 hours.

HYDROGEN PEROXIDE, HYDROGEN DIOXIDE, OR HYDROXYL.

$$H_2O_2 = 34{\cdot}02.$$

This substance is largely used in commerce and is commonly sold as of "10 volume" and "20 volume" strength, meaning thereby that the solution, when fully decomposed, yields ten times and twenty times its own volume respectively of oxygen. A still stronger preparation ("Perhydrol") can now be obtained which yields 100 times its own volume of oxygen: it contains 30 per cent. of H_2O_2.

Kingzett‡ has shown that the best method of determining hydrogen peroxide is to add to its solution, strongly acidified with sulphuric acid, some potassium iodide, and to titrate the iodine set free with sodium thiosulphate and starch solution. The reaction is as follows:—

$$2HI + H_2O_2 = 2H_2O + I_2.$$

The function performed by the sulphuric acid is difficult of explanation, but the want of uniformity in the reaction experienced by many operators no doubt has arisen from the use of insufficient acid.

Method of Procedure: Mix 10 c.c. of the peroxide solution to be examined with about 30 c.c. of dilute sulphuric acid (1 : 2) in a beaker, add crystals of potassium iodide in sufficient quantity, and after standing five minutes titrate the liberated iodine with $^N/_{10}$ thiosulphate and starch. The peroxide solution should not exceed the strength of 2 volumes; if stronger, it must be diluted proportionately before the titration.

* Fowler "*Sewage Works Analyses*," p. 83.

† Many chemists incubate at 80° F. ‡ *J. C. S.* 1880, 792.

In the case of a very weak solution it will be advisable to titrate with $^N/_{100}$ thiosulphate.

1 c.c. $^N/_{10}$ thiosulphate = 0·0017 gm. H_2O_2 or 0·0008 gm. O.

Carpenter and Nicholson* report a series of experiments on the analysis of hydrogen peroxide, both by the iodine and permanganate methods.

The conclusion they arrive at is that the process of Kingzett is accurate, but in their hands somewhat tedious, owing to slow decomposition towards the end. Kingzett however states that if a volume of strong sulphuric acid equal to the peroxide taken be used, and especially if the dilute solution be slightly warmed, the reaction is complete in a few minutes, and this is my own experience.

A number of experiments have been made by C. Smith† as to the value of titrimetric and gasometric methods of ascertaining the amount of oxygen in H_2O_2, if it contains any preservative such as glycerin, boric acid, boroglycerin, salicylic acid, etc. The result was to show that the iodine and thiosulphate method gives accurate results with any of the preservatives tried, and in the presence of large proportions of glycerin, whereas the permanganate methods both titrimetric and gasometric were valueless.

The free acid in hydrogen peroxide solutions can be determined with sufficient accuracy for all practical purposes by direct titration in the cold with standard caustic alkali, using phenolphthalein as indicator.‡

Sodium Peroxide.

$Na_2O_2 = 78.$

L. Archbutt|| gives the results of some experiments on the determination of the available oxygen in this substance, and found that a near approximation to the truth could be obtained by simple titration with permanganate, the peroxide (one or two decigrams) being added to cold water acidified with H_2SO_4 contained in a white dish, and $^N/_{10}$ permanganate dropped in with stirring until the colour became permanent; but a more exact method would be to add a known weight of the peroxide to an excess of $^N/_{10}$ permanganate, previously mixed with dilute H_2SO_4, and titrate for the excess of permanganate with $^N/_{10}$ oxalic acid. Archbutt, however, prefers to use the nitrometer, and recommends the following procedure: about 0·25 gm. of the substance is placed in the dry tube of the nitrometer flask, and in the flask itself about 5 c.c. of pure water, containing in suspension a few milligrams of precipitated cobalt sesqui-oxide; this latter reagent brings about

* *Analyst*, **9**, 36. † *C. N.* **80**, 194. ‡ Brown, *The Analyst*, **35**, 1910, 497.

|| *Analyst*, **20**, 5.

a rapid and complete decomposition of the peroxide, the volume of oxygen evolved being the available oxygen in the sample.

PHOSPHORIC ACID AND PHOSPHATES.

$P_2O_5 = 142{\cdot}08$.

THE determination of phosphoric acid volumetrically may be done with more or less accuracy by a variety of processes, among which may be mentioned that of Mohr as lead phosphate; the indirect method as silver phosphate (the excess of silver being found by thiocyanate); by standard uranium nitrate or acetate; by Pemberton's method as phospho-molybdate; or, when existing only as monocalcic phosphate, by standard alkali, as recommended by Mollenda or Emmerling. These processes are mainly useful in the case of fertilizers, or the raw phosphates from which manures are manufactured, and for P_2O_5 in urine, etc. For the purpose mentioned, that is to say, when in combination with alkali or alkaline earthy bases and moderate quantities of iron or alumina, phosphoric acid may be determined volumetrically with very fair accuracy, and with much greater rapidity than by gravimetric means as usually carried out.

1. Precipitation as Uranium Phosphate in Acetic Acid Solution.

This method is based on the fact that when uranium acetate or nitrate is added to a neutral solution of tribasic phosphoric acid, such, for instance, as sodium orthophosphate, the whole of the phosphoric acid is thrown down as yellow uranium phosphate Ur_2O_3, P_2O_5+Aq. Should the solution, however, contain free mineral acid, it must be neutralized with an alkali, and an alkaline acetate added, together with excess of free acetic acid. In case of using ammonia and ammonium acetate, the whole of the phosphoric acid is thrown down as double phosphate of uranium and ammonia, having a light lemon colour, and the composition Ur_2O_3 $2(NH_4O)$, P_2O_5+Aq. When this precipitate is washed with hot water, dried and ignited, the ammonia is entirely dissipated leaving uranium phosphate, which possesses the formula Ur_2O_3, P_2O_5, and contains in 100 parts 78·71 of uranium oxide and 21·29 of phosphoric acid. In the presence of fixed alkalies, instead of ammonia, the precipitate consists simply of uranium phosphate. By this method phosphoric acid may be completely removed from all the alkalies and alkaline earths; also, with a slight modification, from iron; not, however, satisfactorily from alumina when present in any quantity.

The details of the gravimetric process were fully described by me,* and immediately after the publication of that article, while employed in further investigation of the subject, I devised the

* *C. N.* 1, 97, 122.

volumetric method now to be described. Since that time it has come to my knowledge that Neubauer* and Pincus† had independently of each other and of myself arrived at the same process. This is not to be wondered at, if it be considered how easy the step is from the ordinary determination by weight to that by measure, when the delicate reaction between uranium and potassium ferrocyanide is known. Moreover, the great want of a really good volumetric process for phosphoric acid determination in place of those hitherto used has been felt by all who have had anything to do with the subject, and consequently the most would be made of any new method possessing so great a claim to accuracy as the gravimetric determination of phosphoric acid by uranium undoubtedly does.

Conditions under which approximate accuracy may be ensured.—Objections have been urged, not without reason, that this process is inaccurate, because varying amounts of saline substances have an influence upon the production of colour with the indicator. Again, that very different shades of colour occur with lapse of time. This is all true, and the method is unfortunately one of that class which requires uniform conditions; but when the source of irregularities is known, it is not difficult to obviate them. Therefore, it is absolutely essential that the standardizing of the uranium solution should be done under the same conditions as the analysis. For instance, a different volume of uranium solution will be required to give the colour in the presence of salts of ammonia from that which would be necessary with the salts of the fixed alkalies or alkaline earths. But if the standard solution is purposely adjusted with ammonia salts present in about the same proportion, the difficulties are less. Fortunately this can easily be done, and as the chief substances requiring analysis are more or less ammoniacal in their composition, such as urine, manures, etc., no practical difficulty need occur.

Excessive quantities of alkaline or earthy salts modify the colour, but especially is it so with acetate or citrate of ammonia. For this reason it is necessary to ensure the complete washing of the citromagnesium precipitate, where that method of separating P_2O_5 is adopted previous to titration. With all my experience of this method I cannot contend that it is an absolutely accurate one, but it is nevertheless a very rapid and convenient one for manure manufacturers in testing superphosphates and other phosphatic fertilizers.

2. Determination of Phosphoric Acid in combination with Alkali Bases, or in presence of small quantities of Alkaline Earths.

The necessary materials are—

(*a*) A standard solution of uranium 1 c.c. $=0{\cdot}005$ gm. P_2O_5.

* *Archiv. für wissenschäftliche Heilkunde.*, **4**, 228. † *Journal für Prakt. Chem.* **76**, 104.

(*b*) A standard solution of tribasic phosphoric acid.

(*c*) A solution of sodium acetate in dilute acetic acid, made by dissolving 100 gm. of sodium acetate in water, adding 50 c.c. of glacial acetic acid, and diluting to 1 litre. Exact quantities are not necessary.

(*d*) A freshly prepared solution of potassium ferrocyanide, or some finely powdered pure crystals of the same salt.

Standard Solution of Uranium.—This solution may consist either of uranium nitrate or acetate.* An approximate solution is obtained by using about 35 gm. of either salt to the litre. In using uranium nitrate it is imperative that the sodium acetate should be added in order to avoid the possible occurrence of free nitric acid in the solution. With acetate, however, it may be omitted at the discretion of the operator, but it is important that the method used in standardizing the uranium be invariably adhered to in the actual analysis. The solution should be perfectly clear and free from basic salt. Whether made from acetate or nitrate, it is advisable to include about 50 c.c. of pure glacial acetic, or a corresponding quantity of weaker acid, to each litre of solution; exposure to light has then less reducing action.

My own practice is to use in all cases acetate solution, and dispense entirely with the addition of sodium acetate.

3. Titration of the Uranium Solution.

Standard Phosphoric Acid.—When the uranium solution is not required for phosphate of lime, it may be titrated upon ammonio-sodium phosphate (microcosmic salt) as follows:—5·88 gm. of the crystallized, non-effloresced salt (previously powdered and pressed between bibulous paper to remove any adhering moisture) are weighed, dissolved in water, and diluted to 1 litre. 50 c.c. of this solution will represent 0·1 gm. of P_2O_5.†

METHOD OF PROCEDURE: 50 c.c. of this solution are measured into a small beaker 5 c.c. sodium acetate solution added if uranium nitrate is to be used, and the mixture heated to 90° or 100° C. The uranium solution is then delivered in from a burette, divided into $\frac{1}{10}$ c.c., until a test taken shall show the slight predominance of uranium. This is done by spreading a drop or two of the hot mixture upon a clean white level plate, and bringing in contact with the middle

* Some operators object to the use of acetate, the reason for which I cannot understand. It stands to reason that, as with the use of nitrate there has to be a considerable quantity of sodium acetate used to prevent the formation of free HNO_3, the same conditions practically occur as if uranium acetate was used. The real reason, I believe is, that it is rather difficult to procure pure acetate. In the course of some thousands of titrations, I have found no advantage in using nitrate, and acetate needs no corrector to complicate the process as is the case with nitrate.

† W. B. Giles, who has had great experience in the determination of phosphoric acid in various forms, has called my attention to dihydric potassium phosphate, KH_2PO_4, as an excellent form of salt for a standard solution, The sample sent to me was in beautifully formed crystals which do not alter on exposure to the air, and makes a solution which keeps clear. Every one knows how unsatisfactory sodium phosphate is, both as to its state of hydration and its keeping qualities in solution; the microcosmic salt is better, but is open to objection on the score of indefinite hydration. If the potassium salt is used, a standard solution of the proper strength is made by dissolving 3·836 gm. in a litre.

of the drop a thin glass rod moistened with the freshly made solution of ferrocyanide, or a dust of the powdered salt. The production of a faint brown tinge shows an excess of uranium, the slightest amount of which produces a brown precipitate of uranium ferrocyanide.

A second or third titration is then made in the same way, so as to arrive at the exact strength of the uranium solution, which is then diluted and re-titrated, until exactly 20 c.c. are required to produce the necessary reaction with 50 c.c. of phosphate.

Suppose 18·7 c.c. of the uranium solution have been required to produce the colour with 50 c.c. of phosphate solution, then every 18·7 c.c. will have to be diluted to 20 c.c. in order to be of the proper strength, or 935 to 1000. After dilution, two or three fresh trials must be made to ensure accuracy.

It is of considerable importance that the actual experiment for determining phosphoric acid by means of the uranium solution should be made with about the same bulk of fluid that has been used in standardizing the solution, and the same depth of colour aimed at in each case. Hence the proportions here recommended have been chosen, so that 50 c.c. of liquid shall contain 0·1 gm. of P_2O_5.

Standard Phosphoric Acid corresponding volume for volume with Standard Uranium.—This solution is obtained by dissolving 14·720 gm. of microcosmic salt in a litre, and is two and a half times the strength of the solution before described; it is used for residual titration in case the required volume of uranium is overstepped in any given analysis.

A little practice enables the operator to tell very quickly the precise point; but it must be remembered that when the two drops are brought together for the production of the chocolate colour, however faint it seems at first, if left for some little time the colour increases considerably; but this has no effect upon the accuracy of the process, since the original standard of the solution has been based on an experiment conducted in precisely the same way.

Method of Procedure: In determining unknown quantities of P_2O_5 it is necessary to have an approximate knowledge of the amount in any given material, so as to fulfil as nearly as possible the conditions laid down above; that is to say, 50 c.c. of solution shall contain about 0·1 gm. P_2O_5, or whatever other proportion may have been used in standardizing the uranium.

The compound containing the P_2O_5 to be determined is dissolved in water; if no ammonia is present, 1 c.c. of 10 per cent, solution is dropped in and neutralized with the least possible quantity of acetic acid (also 5 c.c. of sodium acetate if uranium nitrate has to be used), and the volume made up to about 50 c.c., then heated to about 90° C. on the water bath, and the uranium solution delivered in cautiously, with frequent testing as above described, until the faint brown tinge appears.

The first trial will give roughly the amount of solution required and taking that as a guide, the operator can vary the amount of liquid for the final titration, should the proportions be found widely differing from those under which the strength of the uranium was originally fixed.

Each c.c. of uranium solution $=0·005$ gm. P_2O_5.

4. Determination of Phosphoric Acid in combination with Lime and Magnesia (Bones, Bone Ash, Soluble Phosphates, and other Phosphatic Materials free from Iron and Alumina).

The procedure in these cases differs from the foregoing in two respects only; that is to say, the uranium solution is preferably standardized by tribasic calcium phosphate; and in the process of titration it is necessary to add nearly the full amount of uranium required before heating the mixture, so as to prevent the precipitation of calcium phosphate, which is apt to occur in acetic acid solution when heated; or the modification adopted by Fresenius Neubauer, and Luck, may be used, which consists in reversing the process by taking a measured volume of uranium, and delivering into it the solution of phosphate until a drop of the mixture ceases to give a brown colour with ferrocyanide. This plan gives, however, much more trouble, and possesses no advantage on the score of accuracy, because in any case at least two titrations must be performed, and the first being made somewhat roughly, in the ordinary way, shows within 1 or 2 c.c. the volume of standard uranium required; and in the final trial it is only necessary to add at once nearly the full quantity, then heat the mixture, and finish the titration by adding a drop or two of uranium at a time until the required colour is obtained.

This reversed process is strongly advocated by many operators, but except in rare instances I fail to see its superiority to the direct method for general use. The best modification to adopt in the reverse process is to use invariably an excess of uranium, and to titrate back with standard phosphate solution till the colour disappears; this avoids all the trouble of preparing and cleaning a burette for the solution to be analysed, and if a standard phosphate is made to correspond volume for volume with the uranium, an analysis may always be brought into order at any stage.

Standard Calcium Phosphate.—It is not safe to depend upon the usual preparations of tricalcium phosphate by weighing any given quantity direct, owing to uncertainty as to the state in which the phosphoric acid may exist; therefore, in order to titrate the uranium solution with calcium phosphate, it is only necessary to take rather more than 5 gm. of precipitated pure tricalcium phosphate such as is obtained in commerce, dissolve it in a slight excess of dilute hydrochloric acid, precipitate again with a slight excess of ammonia, re-dissolve in a moderate excess of acetic acid, then dilute to a litre; by this means is obtained a solution of acid monocalcium phosphate, existing under the same conditions as in the actual analysis. In order to ascertain the exact amount of tribasic phosphoric acid present in a given measure of this solution, two portions of 50 c.c. each are measured into two beakers, each holding about half a litre. A slight excess of solution of uranium acetate or nitrate is then added to each, together with about 10 c.c.

of the acetic solution of sodium acetate; they are then heated to actual boiling on a hot-plate or sand-bath, the beakers filled up with boiling distilled water, and then set aside to settle, which occurs very speedily. The supernatant fluid should be faintly yellow from excess of uranium. When perfectly settled, the clear liquid is poured off as closely as possible without disturbing the precipitate, and the beakers again filled up with boiling water. The same should be done a third time, when the precipitates may be brought on two filters, and need very little further washing.

When the filtration is complete, the filters are dried and ignited apart from the precipitate, taking care to burn off all carbon. Before being weighed, however, the uranium-phosphate must be moistened with strong nitric acid, dried perfectly in the water-bath or oven, and again ignited; at first very gently, then strongly, so as to leave a residue of a pure light lemon colour when cold. This is uranium phosphate Ur_2O_3, P_2O_5, the percentage composition of which is 78·71 of uranium oxide, and 21·29 of phosphoric acid.

The two precipitates are accurately weighed, and should agree to within a trifle. If they differ, the mean is taken to represent the amount of P_2O_5 in the given quantity of tricalcium phosphate, from which may be calculated the strength of the solution to be used as a standard. Of course any other accurate method of determining the P_2O_5 may be used in place of this.

The actual standard required is 5 gm. of pure tricalcium phosphate per litre; and it should be adjusted to this strength by dilution, after the actual strength has been found. In this way is obtained a standard which agrees exactly with the analysis of a superphosphate or other similar manure.

Standard Uranium Solution.—This is best adjusted to such strength that 25 c.c. are required to give the faint chocolate colour with ferrocyanide, when 50 c.c. of the standard acetic solution of calcium phosphate are taken for titration. Working in this manner each c.c. of uranium solution represents 1 per cent. of soluble tricalcium phosphate, when 1 gm. of a fertilizer is taken for analysis, because 50 c.c. of the calcium phosphate will contain monocalcium phosphate equal to 0·25 gm. of $Ca_3P_2O_8$ and will require 25 c.c. of uranium solution to balance it.

These standards are given as convenient for fertilizers, but they may be modified to suit any particular purpose.

THE METHOD WITH SUPERPHOSPHATES FREE FROM FE AND AL, EXCEPT IN MERE TRACES, is as follows:—10 gm. of the substance are weighed, placed in a small glass mortar and gently broken down by the pestle, cold water being used to bring it to a smooth cream. The material should not be ground or rubbed hard, which might cause the solution of some insoluble phosphate in the concentrated mixture. The creamy substance is washed gradually without loss into a measuring flask marked at 503·5 c.c., the 3·5 c.c. being the space occupied by the insoluble matters in an ordinary 25 to 30 per cent. superphosphate. The flask is filled to the mark with cold water, and shaken every few minutes during about half an hour. A portion is then filtered through a dry filter into a dry beaker, and 50 c.c. (= 1 gm. of fertilizer) measured into a beaker holding about 100 c.c. Sufficient

10 per cent. ammonia is then added to precipitate the monocalcium phosphate in the form of $Ca_3P_2O_8$ (in all ordinary superphosphates there is enough Ca present as sulphate to ensure this, and four or five drops of ammonia generally suffice to effect the precipitation). Acetic acid is then added in just sufficient quantity to render the liquid clear. Should traces of gelatinous $AlPO_4$ or $FePO_4$ appear at this stage, the liquid will be slightly opalescent; but this may be disregarded if only slight, as the subsequent heating will enable the uranium to decompose it. If more than traces are present, the method will not be accurate, and recourse must be had to separation by the citro-magnesium solution.

While the liquid is still cold, a measured volume of the standard uranium is run in with stirring, and drops are occasionally taken out with a glass rod, and brought in contact with some ferrocyanide indicator spotted on a white plate until a faint colour appears. The beaker is then placed in the water-bath for a few minutes, and again the mixture tested with the indicator; after heating in this way the testing ought to show no colour. More uranium is then added with stirring, and drop by drop till the proper reaction occurs. This titration is only a guide for a second, which may be made more accurate by running in at once very nearly the requisite volume of uranium.

This operation may be reversed, if so desired, by making the clear solution of phosphate up to a definite volume (say 60 c.c.), and running it from a burette into a measured volume of uranium until a test taken shows no colour.

5. Determination of Phosphoric Acid in Minerals or other materials containing Iron, Alumina, or other interfering substances.

In order to make use of any volumetric process for this purpose the phosphoric acid must be separated. As has been already described, this may be done either as molybdenum phosphate followed by solution in NH_3, and again precipitated with ordinary magnesia mixture, or direct separation by the citro-magnesium mixture described below. In either case the ammonio-magnesium salt is dissolved in the least possible quantity of nitric or hydrochloric acid, neutralized with ammonia, acidified with acetic acid, and the titration with uranium carried out as before described.

6. Pemberton's Molybdic Method.

This method* is one which requires great delicacy of manipulation, but gives excellent results with all the alkali or earthy phosphates.

The latest form of the method, "Pemberton's New Molybdic Method Modified," † is as follows :—

The solutions required are :

Molybdate Solution. Dissolve 100 gm. of molybdic acid in 144 c.c. of ammonia, sp. gr. 0·90, and 271 c.c. of water; slowly, and with constant stirring, pour the solution thus obtained into 489 c.c. of nitric acid (sp. gr. 1·42), and 1148 c.c. of water. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

For use add to 100 c.c. of this solution 5 c.c. of nitric acid, sp. gr. 1·42. Filter each time before using.

* *J. Am. C. S.* 1894, 278. † *Bulletin* No. 107, U. S. Dept. Agric.

Standard Potassium Hydroxide Solution. This solution contains 18·17106 gm. of potassium hydroxide to the litre. It is prepared by diluting 323·81 c.c. of normal potash (which has been freed from carbonates by barium hydroxide) to one litre. 100 c.c. of the solution should neutralize 32·38 c.c. of normal acid. One c.c. of this is equal to 0·001 gm. of P_2O_5, or 1 per cent. if 0·1 gm. of the substance is taken for analysis. Normal soda may be used instead of potash.

Standard Nitric Acid Solution. This solution should correspond in strength to the standard alkali solution, or may be one half that strength. It is standardized by titrating against that solution, using phenolphthalein as indicator. Any mineral acid may be used.

If a soluble phosphate is to be analysed, dissolve 1 gm. in water to 250 c.c. 25 c.c. of this solution, representing 0·1 gm. of the substance, is taken for analysis. If the phosphate is in an insoluble compound or organic substance, 2 gm. are treated by one of the methods given below. After solution, cool, dilute to 200 or 250 c.c., mix and pour on a dry filter.

Total Phosphoric Acid. (*a*) Dissolve in 30 c.c. of concentrated nitric acid and a small quantity of hydrochloric acid and boil until organic matter is destroyed.

(*b*) Evaporate with 5 c.c. of magnesium nitrate, ignite, and dissolve in hydrochloric acid.

(*c*) Add 30 c.c. of concentrated hydrochloric acid, heat, and add cautiously, in small quantities at a time, about 0·5 gm. of finely pulverized potassium chlorate to destroy organic matter.

(*d*) Dissolve in from 15 to 30 c.c. of strong hydrochloric acid and from 3 to 10 c.c. of nitric acid. This method is recommended for fertilizers containing much iron or aluminium phosphate.

DETERMINATION.—(1) For percentages of 5 or below use an aliquot volume corresponding to 0·4 gm. of substance; for percentages between 5 and 20 use a volume corresponding to 0·2 gm. of substance, and for percentages above 20 use a volume corresponding to 0·1 gm. of substance. Add from 5 to 10 c.c. of nitric acid, depending on the method of solution (or the equivalent in ammonium nitrate), nearly neutralize with ammonia, dilute to from 75 to 100 c.c., heat in water-bath to from 60° to 65° C., and for percentages below 5 add from 20 to 25 c.c. of freshly filtered molybdate solution. For percentages between 5 and 20 add from 30 to 35 c.c. of molybdate solution; stir, let stand about fifteen minutes, filter *at once* wash once or twice with water by decantation, using from 25 to 30 c.c. each time, agitating the precipitate thoroughly and allowing to settle; transfer to filter and wash with cold water until two fillings of the filter do not greatly diminish the colour produced with phenolphthalein by one drop of the standard alkali. Transfer precipitate and filter to beaker or precipitating vessel, dissolve in small excess of standard alkali, add a few drops of phenolphthalein solution, and titrate with standard acid.

(2) Proceed as directed in (1), with this exception: Heat in a water-bath at 45° to 50° C., add the molybdate solution, and allow to remain in the bath with occasional stirring for thirty minutes.

(3) Proceed as in (1) to the point where the solution is ready to place in the water-bath. Then cool solution to room temperature, add molybdate solution at the rate of 75 c.c. for each 0·1 gm. of phosphoric acid present, place the stoppered flask containing the solution in a shaking apparatus and shake for thirty minutes at room temperature, filter at once, wash, and titrate as in preceding method.

Water-soluble Phosphoric Acid. Place 2 gm. of the sample on a 9-cm. filter, wash with successive small portions of water, allowing each portion to pass through before adding more, until the filtrate measures about 250 c.c. If the filtrate be turbid, add a little nitric acid. Make up to any convenient definite volume, mix well, use an aliquot portion of the solution corresponding to 0·2 or 0·4 gm., add 10 c.c. of concentrated nitric acid and ammonia until a slight permanent precipitate is formed, dilute to 60 c.c., and proceed as under the preceding method (1).

Citrate-insoluble Phosphoric Acid. Make the solution according to the

directions given before and determine the phosphoric acid in an aliquot volume corresponding to 0·4 gm., as directed for total phosphates.

Determination in Acidulated Samples. Heat 100 c.c. of strictly neutral ammonium citrate solution of 1·09 sp. gr. to 65° C. in a flask placed in a warm water-bath, keeping the flask loosely stoppered to prevent evaporation. When the citrate solution in the flask has reached 65° C. drop into it the filter containing the washed residue from the water-soluble phosphate determination, close tightly with a smooth rubber stopper, and shake violently until the filter paper is reduced to a pulp. Place the flask in the bath and maintain it at such a temperature that the contents of the flask will stand at exactly 65° C. Shake the flask every five minutes.

At the expiration of exactly thirty minutes from the time the filter and residue are introduced, remove the flask from the bath and immediately filter the contents as rapidly as possible; wash thoroughly with water at 65° C. Then proceed as under (*a*) or (*b*).

(*a*) Transfer the filter and its contents to a crucible, ignite until all organic matter is destroyed, add from 10 to 15 c.c. of strong hydrochloric acid, and digest until all phosphate is dissolved, or (*b*) return the filter with contents to digestion flask, add from 30 to 35 c.c. of strong nitric acid, and from 5 to 10 c.c. of strong hydrochloric acid, and boil until all phosphate is dissolved. Dilute to 200 c.c., mix well, and pass through a dry filter. Take a definite portion of the filtrate and proceed as under *total phosphoric acid.*

Determination of Non-acidulated Samples. Treat 2 gm. of the phosphatic material without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, etc.), the residue, insoluble in ammonium citrate, is to be dissolved by the treatment described under (*b*), or by digestion with concentrated sulphuric acid in the presence of a small quantity of sodium or potassium nitrate.

Citrate-soluble Phosphoric Acid. The sum of the water-soluble and citrate-insoluble subtracted from the total phosphoric acid, gives the citrate-soluble phosphoric acid.

Richardson* states that when phosphoric acid is determined in acid phosphate by the Pemberton volumetric method or it usual modifications, the results do not agree with those obtained gravimetrically by the A. O. A. C. method, and the error frequently amounts to + 1 per cent. P_2O_5.

The disturbing substance is probably sulphuric acid, and if this be removed by barium chloride, the volumetric method may be applied and accurate results obtained.

Richardson recommends the following procedure:

Weigh 2 gm. into a 250 c.c. flask, digest by boiling with 30 c.c. of concentrated nitric acid and 5 c.c. concentrated hydrochloric acid, then add 10 c.c. water and boil for five minutes. Add 25 to 30 c.c. of 10 per cent. barium chloride, cool, and make up to volume. Filter through a dry filter, rejecting the first portion of the filtrate, and take 25 c.c. for the determination. From this point on follow the Pemberton Method as above.

7. Determination of Phosphoric Acid by Silver Nitrate (Holleman).†

J. M. Wilkie‡ has modified Holleman's method, in which phosphoric acid or an alkali-metal phosphate is converted to the di-alkali metal salt by means of caustic soda, the silver phosphate precipitated in presence of sodium acetate, and the residual silver determined in the filtrate by Volhard's method. This method usually gives high results, but the following mode of operating gives accurate results:

* *J. A. C. S.* **29**, 1314, and Schimpf, "*Volumetric Analysis*," p. 320.

† *Z. a. Chem.*, **33**, 185, and *J. S. C. I.* 1894, 763 and 843.

‡ *J. S. C. I.* 1910, 794.

Phenolphthalein is added to the solution containing the phosphate, then strong caustic soda till the liquid is just pink, when the colour is discharged by dilute nitric acid, added drop by drop. In presence of calcium the precipitated phosphate is the best indicator, nitric acid being added until the precipitate is just dissolved. Excess of silver solution is next added, followed by 10 c.c. of approximately $^{N}/_{10}$ sodium acetate; then approximately $^{N}/_{10}$ caustic soda is run in, while shaking, till the liquid is faintly alkaline to phenolphthalein. Two c.c. of $^{N}/_{10}$ sulphuric acid are added to this solution, which is diluted to 150 c.c., mixed, filtered, and the silver in the solution determined by Volhard's method. The method is not available in the presence of appreciable amounts of aluminium or iron. Chlorides must be allowed for, but may be got rid of by adding excess of sulphuric acid to the phosphate solution and evaporating at 100° C. The determination is made as above, after addition of nitric acid.

8. Other Volumetric Methods for the determination of Phosphoric Acid.

Several methods depending upon alkalimetry have been suggested, but beyond those quoted under Phosphoric Acid, p. 114, I have found none easy or reliable in practice.

A. Grete* titrates phosphoric acid in acid solution with alkaline molybdate solution in the presence of glue. It is claimed that this method has been thoroughly tested in practice since 1888, and that 20 determinations can be made in an hour, with results equal in accuracy to those obtained by the gravimetric process.

Two iodimetric methods recently described depend upon the interaction of standard sodium hypobromite solution in the presence of potassium iodide (1) with ammonium phospho-molybdate (P. Artmann)† and (2) with ammonium magnesium phosphate (R. Brandis).‡

SILVER.

Ag=107·88.

1 c.c. (or 1 dm.) $^{N}/_{10}$ sodium chloride=0·010788 gm. (or 0·10788 grn.) Silver; also 0·016989 gm. (or 0·16989 grn.) Silver nitrate.

1. Precipitation with $^{N}/_{10}$ Sodium Chloride (Gay Lussac).

The determination of silver is precisely the converse of the operations described under Chlorine (p. 175), and the process may either be concluded by adding the sodium chloride till no further precipitate is produced, or potassium chromate may be used as an indicator. In the latter case, however, it is advisable to add the salt solution in excess, then a drop or two of chromate, and titrate residually with $^{N}/_{10}$ silver, till the red colour produced, is for the excess of sodium chloride.

2. By Ammonium Thiocyanate.

The principle of this method is fully described on page 145, et. seq., and need not further be alluded to here. The author of

* *Ber.* 1909, **42**, 3106, and *J. S. C. I.*, 1909, 1105.

† *Z. a. Chem.* 1910, **49**, 1, and *J. S. C. I.* 1910, 455.

‡ *Z. a. Chem.* 1910, **49**, 152, and *J. S. C. I.* 1910, 455.

the method (Volhard) states that comparative tests made by this method and by that of Gay Lussac gave equally exact results, both being controlled by cupellation, but claims for this process that the end of the reaction is more easily distinguished, and that there is no labour of shaking, or danger of decomposition by light, as in the case of chloride. My own experience fully confirms this. The method is now adopted largely in place of Gay Lussac's for silver assays.

3. Determination of Silver, in Ores and Alloys, by Starch Iodide (Method of Pisani and F. Field).

If a solution of blue starch iodide be added to a neutral solution of silver nitrate, while any of the latter is in excess the blue colour disappears, the iodine entering into combination with the silver; as soon as all the silver is thus saturated, the blue colour remains permanent, and marks the end of the process. The reaction is very delicate, and the process is more especially applicable to the analysis of ores and alloys of silver containing lead and copper, but not mercury, tin, iron, manganese, antimony, arsenic, or gold in solution.

The solution of starch iodide, devised by Pisani, is made by rubbing together in a mortar 2 gm. of iodine with 15 gm. of starch and about 6 or 8 drops of water, putting the moist mixture into a stoppered flask, and digesting in a water-bath for about an hour, or until it has assumed a dark bluish-grey colour; water is then added till all is dissolved. The strength of the solution is then ascertained by titrating it with 10 c.c. of a solution of silver containing 1 gm. in the litre, to which a portion of pure precipitated calcium carbonate is added; the addition of this latter removes all excess of acid, and at the same time enables the operator to distinguish the end of the reaction more accurately. The starch iodide solution should be of such a strength that about 50 c.c. are required for 10 c.c. of the silver solution (=0·01 gm. silver).

F. Field*, who discovered the principle of this method simultaneously with Pisani, used a solution of iodine in potassium iodide with starch. Those who desire to make use of this plan can use the $^{N}/_{10}$ and $^{N}/_{100}$ solutions of iodine described on p. 129.

In the analysis of silver containing copper, the solution must be considerably diluted in order to weaken the colour of the copper; a small measured portion is then taken, calcium carbonate added, and starch iodide till the colour is permanent. It is best to operate with from 60 to 100 c.c., containing not more than 0.02 gm. silver; when the quantity is much greater than this, it is preferable to precipitate the greater portion with $^{N}/_{10}$ sodium chloride, and to complete with starch iodide after filtering off the chloride. When lead is present with silver in the nitric acid solution, add sulphuric acid, and filter off the lead sulphate, then add calcium carbonate to neutralize excess of acid, filter again if necessary, then add fresh carbonate and titrate as described above.

* *C. N.* 2. 17.

4. Assay of Commercial Silver (Plate, Bullion, Coin, etc.). Gay Lussac's Method modified by J. G. Mulder.

For more than thirty years Gay Lussac's method of determining silver in its alloys has been practised intact, at all the European mints, under the name of the "humid method," in place of the old system of cupellation. During that time it has been regarded as one of the most exact methods of quantitative analysis. The exhaustive researches of Mulder, however, have shown that it is capable of even greater accuracy than has hitherto been supposed.

The principle of the process is the same as described on p. 141, depending on the affinity which chlorine has for silver in preference to all other substances, and resulting in the formation of silver chloride, a compound insoluble in dilute acids, and which readily separates itself from the liquid in which it is suspended.

The plan originally devised by the illustrous inventor of the process for assaying silver, which is still followed, is to consider the weight of alloy taken for examination to consist of 1000 parts, and the question is to find how many of these parts are pure silver. This empirical system was arranged for the convenience of commerce, and being now thoroughly established, it is the best plan of procedure. If, therefore, a standard solution of salt be made of such strength that 100 c.c. will exactly precipitate 1 gm. of silver, it is manifest that each $\frac{1}{10}$ c.c. will precipitate 1 mgm. or $\frac{1}{1000}$ part of the gram taken; and consequently in the analysis of 1 gm. of any alloy containing silver, the number of $\frac{1}{10}$ c.c. required to precipitate all the silver out of it would be the number of thousandths of pure silver contained in the specimen.

In practice, however, it would not do to follow this plan precisely, inasmuch as neither the measurement of the standard solution nor the ending of the process would be gained in the most exact manner; consequently, a decimal solution of salt, one-tenth the strength of the standard solution, is prepared, so that 1000 c.c. will exactly precipitate 1 gm. of silver, and, therefore, 1 c.c. 1 mgm.

The silver alloy to be examined (the composition of which must be approximately known) is weighed so that about 1 gm. of pure silver is present: it is then dissolved in pure nitric acid by the aid of a gentle heat, and 100 c.c. of standard solution of salt added from a pipette in order to precipitate exactly 1 gm. of silver; the bottle containing the mixture is then well shaken until the silver chloride has curdled, leaving the liquid clear.

The question is now: Which is in excess, salt or silver? A drop of decimal salt solution is added, and if a precipitate be produced 1 c.c. is delivered in, and after clearing, another, and so on as long as a precipitate is produced. If on the other hand, the one drop of salt produced no precipitate, showing that the pure silver present was less than 1 gm., a decimal solution of silver is used, prepared by dissolving 1 gm. pure silver in pure nitric acid and diluting to 1 litre. This solution is added after the same manner as the salt

solution just described, until no further precipitate appears; in either case the quantity of decimal solution used is noted, and the results calculated in thousandths for 1 gm. of the alloy.

The process thus shortly described is that originally devised by Gay Lussac, and it was taken for granted that, when equivalent chemical proportions of silver and sodium chloride were brought thus in contact, every trace of the metal was precipitated from the solution, leaving sodium nitrate and free nitric acid only in solution. The researches of Mulder, however, go to prove that this is not strictly the case, but that when the most exact chemical proportions of silver and salt are made to react on each other, and the chloride has subsided, a few more drops of either salt or silver solution will produce a further precipitate, indicating the presence of both silver nitrate and sodium chloride in a state of equilibrium, which is upset on the addition of either salt or silver. Mulder decides, and no doubt rightly, that this peculiarity is owing to the presence of sodium nitrate, and varies somewhat with the temperature and state of dilution of the liquid.

It therefore follows that when a silver solution is carefully precipitated, first by concentrated and then by dilute salt solution, until no further precipitate appears, the clear liquid will at this point give a precipitate with dilute silver solution; and if it be added till no further cloudiness is produced, it will again be precipitable by dilute salt solution.

EXAMPLE: Suppose that in a given silver analysis the decimal salt solution has been added so long as a precipitate is produced, and that 1 c.c. (=20 drops of Mulder's dropping apparatus) of decimal silver is in turn required to precipitate the apparent excess, it would be found that when this had been done, 1 c.c. more of salt solution would be wanted to reach the point at which no further cloudiness is produced by it, and so the changes might be rung time after time; if, however, instead of the last 1 c.c. (=20 drops) of salt, half the quantity be added, that is to say 10 drops (=½ c.c.), Mulder's so-called neutral point is reached; namely, that in which, if the liquid be divided in half, both salt and silver will produce the same amount of precipitate. At this stage the solution contains silver chloride dissolved in sodium nitrate, and the addition of either salt or silver expels it from solution.

A silver analysis may therefore be concluded in three ways—

(1) By adding decimal salt solution until it just ceases to produce a cloudiness.

(2) By adding a slight excess of salt, and then decimal silver till no more precipitate appears.

(3) By finding the neutral point.

According to Mulder the latter is the only correct method, and preserves its accuracy at all temperatures up to 56° C. (=133° Fahr.), while the difference between 1 and 3 amounts to ½ a mgm., and that between 1 and 2 to 1 mgm. on 1 gm. of silver at 16° C. (=60·8° Fahr.), and is seriously increased by variation of temperature.

It will readily be seen that much more trouble and care is required by Mulder's method than by that of Gay Lussac, but as a compensation, much greater accuracy is obtained.

On the whole it appears to me preferable to weigh the alloy so that slightly more than 1 gm. of silver is present, and to choose the ending No. 1, adding drop by drop the decimal salt solution until just a trace of the precipitate is seen, and which, after some practice, is known by the operator to be final. It will be found that the quantity of salt solution used will slightly exceed that required by chemical computation; say 100·1 c.c. are found equal to 1 gm. of silver, the operator has only to calculate that quantity of the salt solution in question for every 1 gm. of silver he assays in the form of alloy, and the error produced by the solubility of silver chloride in sodium nitrate is removed.

If the decimal solution has been cautiously added, and the temperature not higher than 17° C. (62° Fahr.), this method of conclusion is as reliable as No. 3, and free from the possible errors of experiment; for it requires a great expenditure of time and patience to reverse an assay two or three times, each time cautiously adding the solutions drop by drop, then shaking and waiting for the liquid to clear, besides the risk of discolouring the silver chloride, which would at once vitiate the results.

The decimal silver solution, according to this arrangement, would seldom be required; if the salt has been incautiously added, or the quantity of alloy too little to contain 1 gm. pure silver, then it is best to add once for all 2, 3, or 5 c.c., according to circumstances, and finish with decimal salt as No. 1, deducting the silver added.

The Standard Solutions and Apparatus.

(*a*) **Standard Salt Solution.**—Pure sodium chloride is readily purchased. It is made by passing HCl gas into a strong solution of common salt, when pure sodium chloride crystallizes out. The crystals are slightly washed with cold water, dried, and heated to dull redness. When cold, 5·419 grams are weighed and dissolved in 1 litre of distilled water at 15° C. 100 c.c. of this solution will precipitate exactly 1 gram of silver. It is preserved in a well-stoppered bottle, and shaken before use.

(*b*) **Decimal Salt Solution.**—100 c.c. of the above solution are diluted to exactly 1 litre with distilled water at 15° C. 1 c.c. will precipitate 0·001 gm. of silver.

(*c*) **Decimal Silver Solution.**—Pure metallic silver is best prepared by galvanic action from pure chloride; and as clean and safe a method as any is to wrap a lump of clean zinc, into which a silver wire is melted, with a piece of wetted bladder or calico, so as to keep any particles of impurity contained in the zinc from the silver. The chloride is placed at the bottom of a porcelain dish, covered with dilute sulphuric acid, and the zinc laid in the middle; the silver wire is bent over so as to be immersed in the chloride. As soon as the acid begins to act upon the zinc the reduction of the chloride commences, and proceeds gradually throughout the mass; the resulting finely-divided silver is well-washed, first with dilute acid, then with hot water, till all acid and soluble zinc salts are removed.

The moist metal is then mixed with a little sodium carbonate, saltpetre, and borax, say about an eighth part of each, dried perfectly, then melted. Mulder recommends that the melting should be done in a porcelain crucible immersed in sand contained in a common earthen crucible; borax is sprinkled over the surface of the sand so that it may be somewhat vitrified, that in pouring out the

silver when melted no particles of dirt or sand may fall into it. If the quantity of metal be small it may be melted in a porcelain crucible over a gas blowpipe.

The molten metal obtained in either case can be poured into cold water and so granulated, or upon a slab of pipe-clay, into which a glass plate has been pressed when soft so as to form a shallow mould. The metal is then washed well with boiling water to remove accidental surface impurities, and rolled into thin strips by a goldsmith's mill, in order that it may readily be cut for weighing. The granulated metal is, of course, ready for use at once without any rolling.

1 gm. of this silver is dissolved in pure dilute nitric acid, and diluted to 1 litre ; each c.c. contains 0·001 gm. of silver. It should be kept from the light.

(*d*) **Dropping Apparatus for Concluding the Assay.**—Mulder constructs a special apparatus for this purpose consisting of a pear-shaped vessel fixed in a stand, with special arrangements for preventing any continued flow of liquid. The delivery tube has an opening of such size that 20 drops measure exactly 1 c.c. The vessel itself is not graduated. As this arrangement is of more service in assay than in general laboratories, it need not be further described here. A small burette divided in $\frac{1}{10}$ c.c. with a convenient dropping tube will answer every purpose, and possesses the further advantage of recording the actual volume of fluid delivered.

The 100 c.c. pipette, for delivering the concentrated salt solution, must be accurately graduated, and should deliver exactly 100 gm. of distilled water at 15° C.

The test bottles, holding about 200 c.c., should have their stoppers well ground and brought to a point, and should be fitted into japanned tin tubes reaching as high as the neck, so as to preserve the precipitated chloride from the action of light, and, when shaken, a piece of black cloth should be placed over the stopper.

(*e*) **Titration of the Standard Salt Solution.**—From what has previously been stated as to the principle of this method, it will be seen that it is not possible to rely absolutely upon a standard solution of salt containing 5·419 gm. per litre, although this is chemically correct in its strength. The real working value must be found by experiment. From 1·002 to 1·004 gm. of absolutely pure silver is weighed on the assay balance, put into a test bottle with about 5 c.c. of pure nitric acid of about 1·2 sp. gr., gently heated in the water or sand bath till it is all dissolved. The nitrous vapours are then blown from the bottle, and it is set aside to cool down to about 16° C. or 60° Fahr.

The 100-c.c. pipette, which should be securely fixed in a support, is then carefully filled with the salt solution, and delivered into the test bottle contained in its case, the moistened stopper inserted, covered over with the black velvet or cloth, and shaken continuously till the chloride has clotted and the liquid become clear ; the stopper is then slightly lifted, and its point touched against the neck of the bottle to remove excess of liquid, again inserted, and any particles of chloride washed down from the top of the bottle by carefully shaking the clear liquid over them. The bottle is then brought under the decimal salt burette, and $\frac{1}{2}$ c.c. added, the mixture shaken, cleared, another $\frac{1}{2}$ c.c. put in and the bottle lifted partly out of its case to see if the precipitate is considerable ; lastly, 2 or 3 drops only of the solution are added at a time until no further opacity is produced by the final drop. Suppose, for instance, that in titrating the salt solution it is found that 1·003 gm. of silver require 100 c.c. concentrated, and 4 c.c. decimal solution, altogether equal to 100·4 c.c. concentrated, then—

$$1{\cdot}003 \text{ silver} : 1{\cdot}000 : 100{\cdot}4 \text{ salt} :: x. \quad x = 100{\cdot}0999.$$

The result is within $\frac{1}{10000}$ of 100·1, which is near enough for the purpose, and may be more conveniently used. The operator therefore knows that 100·1 c.c. of the concentrated salt solution at 15° C. will exactly precipitate 1 gm. silver, and in his examination of alloys calculates accordingly.

In the assay of coin and plate of the English standard, namely, 11·1 silver and 0·9 copper, the weight corresponding to 1 gm. of silver is 1·081 gm. therefore in examining this alloy 1·085 gm. may be weighed.

When the quantity of silver is not approximately known, a preliminary analysis is necessary, which is best made by dissolving $\frac{1}{2}$ or 1 gm. of the alloy in nitric acid, and precipitating very carefully with the concentrated salt solution

from a $\frac{1}{10}$ c.c. burette. Suppose that in this manner 1 gm. of alloy required 45 c.c. salt solution,

$$\begin{array}{ccccccc} \text{salt} & & \text{salt} & & \text{silver} & & \text{silver} \\ 100{\cdot}1 & : & 45 & :\,: & 1 & : & x \end{array}$$

$$x = 0{\cdot}4495$$

$$\text{And } 0{\cdot}4495 : 1{\cdot}003 :\,: 1 : x$$

$$x = 2{\cdot}231.$$

2·231 gm. of this particular alloy are therefore taken for the assay.

Where alloys of silver contain sulphur or gold, with small quantities of tin, lead, or antimony, they are first treated with a small quantity of nitric acid so long as red vapours are disengaged, then boiled with concentrated sulphuric acid till the gold has become compact, set aside to cool, diluted with water, and titrated as above.

Assaying on the Grain System.

It will readily be seen that the process just described may quite as conveniently be arranged on the grain system by substituting 10 grains of silver as the unit in place of the gram; each decem of concentrated salt solution would then be equal to $\frac{1}{10}$ of a grain of silver, and each decem of decimal solution to $\frac{1}{100}$ of a grain.

5. Titration of the Silver Solutions used in Photography.

The silver bath solutions for sensitizing collodion and paper frequently require examination, as their strength is constantly lessening. To save calculation, it is better to use an empirical solution of salt than the systematic one described above.

This is best prepared by dissolving 43 grains of pure sodium chloride in 10,000 grains of distilled water. Each decem (=10 grn.) of this solution will precipitate 0·125 grn. (*i.e.*, $\frac{1}{8}$ grn.) of pure silver nitrate; therefore if one fluid drachm of any silver solution be taken for examination, the number of decems of salt solution required to precipitate all the silver will be the number of grains of silver nitrate in each ounce of the solution.

Example: One fluid drachm of an old nitrate bath was carefully measured into a stoppered bottle, 10 or 15 drops of pure nitric acid and a little distilled water added; the salt solution was then cautiously added, shaking well after each addition until no further precipitate was produced. The quantity required was 26·5 dm = 26½ grains of silver nitrate in each ounce of solution.

Crystals of silver nitrate may also be examined in the same way, by dissolving say 30 or 40 grn. in an ounce of water, taking one drachm of the fluid and titrating as above.

In consequence of the rapidity and accuracy with which silver may be determined when potassium chromate is used as indicator, some may prefer to use that method. It is then necessary to have a standard solution of silver, of the same chemical value as the salt solution; this is made by dissolving 125 grains of pure and dry neutral silver nitrate in 1000 dm. of distilled water; both solutions will then be equal, volume for volume.

Suppose, therefore, it is necessary to examine a silver solution used for sensitizing paper. One drachm is measured, and, if any free acid be present, cautiously neutralized with a weak solution of sodium carbonate; 100 dm. of salt solution are then added with a pipette. If the solution is under 100 grn. to the ounce, the quantity will be sufficient. 3 or 4 drops of chromate solution are then added, and the silver solution delivered from the burette until the red colour

of silver chromate is just visible. If 25·5 dm. have been required, that number is deducted from the 100 dm. of salt solution, which leaves 74·5 dm., or 74½ grains to the ounce.

This method is much more likely to give exact results in the hands of persons not expert in analysis than the ordinary plan by precipitation, inasmuch as, with collodion baths, containing as they always do silver iodide, it is almost impossible to get the supernatant liquid clear enough to distinguish the exact end of the analysis.

SUGARS.

SUGARS belong to the large class of organic bodies known as "carbo-hydrates," of which there are three main classes, viz. :—

(1) The Hexoses, $C_6H_{12}O_6$, including

(i) Glucose, Dextrose or Grape Sugar, which is found in large quantities in grapes (whence its name), and also in the urine of persons suffering from diabetes mellitus. It is the ultimate product of the hydrolysis of starch by a dilute acid.

(ii) Fructose, Laevulose or Fruit Sugar, which, associated with dextrose, is found in the juice of sweet fruits and in honey.

(iii) Galactose, which is produced, together with dextrose, when lactose is hydrolyzed by dilute mineral acids.

All the above reduce Fehling's solution. None of them are affected by boiling with dilute acids.

(2) The Cane-sugar group, $C_{12}H_{22}O_{11}$, including

(i) Sucrose or Cane-Sugar, which is found in the sugar cane, beetroot and maple.

(ii) Lactose or Milk Sugar (cryst. $C_{12}H_{22}O_{11},H_2O$), which is found in the milk of mammals and in various pathological secretions.

(iii) Maltose or Malt sugar (cryst. $C_{12}H_{22}O_{11},H_2O$), which, together with dextrin, is produced by the action of diastase on starch.

(iv) Raffinose, $C_{18}H_{32}O_{16}$ (cryst. $C_{18}H_{32}O_{16}$, $5H_2O$), which is found in beet molasses and in eucalyptus manna.

Lactose and maltose reduce Fehling's solution, but to a less degree than the hexoses. Cane sugar does so only after hydrolysis, but raffinose has no reducing effect on this solution.

All the members of this group are hydrolyzed by heating with dilute mineral acids or by the action of soluble ferments (enzymes), such as diastase (in malt), invertase (in yeast), and ptyalin (in the saliva). Cane sugar in this way becomes converted into a mixture of dextrose and laevulose in equal numbers of molecules, the process being known as "inversion" and the product "invert sugar," as the dextro-rotatory cane sugar solution becomes the laevo-rotatory mixture. By hydrolysis, lactose is converted into dextrose and galactose, maltose into dextrose alone, and raffinose into dextrose, laevulose and galactose.

(3) The Cellulose group $(C_6H_{10}O_5)_n$, including

(i) Cellulose, which forms the membrane of plant cells and of which cotton, wood, etc., mainly consist.

(ii) Starch or Amylum, which is present in the grains of cereals, in potatoes, etc.

(iii) Glycogen or Animal Starch, which is found in the liver in mammalia.

(iv) The Dextrins, produced by heating starch to about 210°, either alone or with a little dilute sulphuric acid; they are intermediate products in the conversion of starch into glucose. The various dextrins are distinguished by their behaviour with iodine. Amylo-dextrin, like starch, gives a blue colour with iodine; erythro-dextrin, which is formed by the partial hydrolysis of amylo-dextrin, a red colour. The succeeding compounds, the achroo-dextrins, give no colour at all.

None of the above reduce Fehling's solution.

By the action of dilute sulphuric acid starch, glycogen, and cellulose are ultimately hydrolyzed to dextrose.

The reducing action of certain sugars, as specified above, on alkaline solutions of copper has been the subject of much careful work by a large number of chemists, both gravimetric and volumetric processes being employed. Both methods are capable of giving good results, but in order to obtain a high degree of accuracy it is essential in every case that certain details of procedure be strictly adhered to.

Kjeldahl maintains that Fehling's solution, however pure its constituents, always undergoes a slight reduction on prolonged heating, especially in strong solution, and he fixes the limit of time for which the liquid should be exposed to the temperature of boiling water at twenty minutes.

1. The conversion of various Sugars into Glucose.

The inversion of cane sugar is carried out as follows: To a solution of sugar containing not more than 25 grams in 100 c.c. add one-tenth of its volume of fuming HCl and heat in a flask, placed in a water-bath, till the contents have acquired the temperature of 68° C., arranging matters so that the operation occupies about 10 minutes. The flask is then removed and cooled. Some operators prefer dilute sulphuric acid and boil the mixture for 5 to 10 minutes. The hydrolysis of lactose requires a longer boiling than this.

Maltose, when heated with dilute acid, gradually becomes hydrolyzed into glucose, the process requiring about 3 or 4 hours at the ordinary pressure. 3 c.c. of concentrated sulphuric acid are added to each 100 c.c. of the solution, which is then heated in a water-bath for 3 or 4 hours. If any dextrin be present, this will also be converted into glucose.

The hydrolysis of the slowly changing sugars may be hastened considerably by heating at increased atmospheric pressure, although some authorities condemn the process. O'Sullivan,* however,

* See Allen's *Commercial Organic Analysis*, Vol. I.

states that a good result with maltose or dextrin is obtained by heating 30 gm. of the substance in 100 c.c. of water containing 1 c.c. of H_2SO_4 for 20 minutes, at a pressure of one additional atmosphere. Allen also gives a handy means of carrying out this method, which consists in using a soda water bottle with rubber stopper through which passes a long glass tube bent at right-angles, and immersed to a depth of 30 inches in mercury contained in a vertical tube of glass or metal. The rubber stopper must be secured by wire, and the bottle heated to boiling in a saturated solution of sodium nitrate, which gives a temperature corresponding to an extra atmosphere.

Of course in all cases where acid has been used for the inversion of sugar, it must be neutralized before the copper titration takes place; this may be done either with sodium or potassium hydrate or carbonate, or calcium carbonate may be used.

Starch from various sources may be hydrolyzed in the same way as the sugars, but it needs a prolonged heating with acid. For approximate purpose 1 gm. of starch should be mixed to a smooth cream with about 30 c.c. of cold water, then 1 c.c. of strong hydrochloric acid added, and the mixture kept at a boiling temperature in an obliquely fixed flask for 8 or 10 hours, replacing the evaporated water from time to time to avoid charring the sugar, and testing with iodine to ascertain when the inversion is complete. The product is glucose.

For the determination of the starch itself a number of processes were tried by Ost,* the one which was found to answer best being that of Sachsse,† slightly modified. In this modification 3 gm. of the starch are heated with 200 c.c. of water and 20 c.c. of hydrochloric acid, specific gravity 1·125 (=5·600 gm. of HCl), for two to three hours *in* a boiling water-bath, using the factor 0·925 to calculate the glucose found in the starch. Longer heating gives results too low, and two hours *on* the water-bath are not sufficient. Slightly higher yields of glucose (89·8 instead of 89·5 per cent.) can be obtained by heating for a much longer period with less starch and acid, but there is no advantage to be gained by the alteration. Oxalic acid gives no better results. Dextrin may be determined in the same manner; also maltose, if 1 gm. of the latter be heated for five hours with 100 c.c. of 1 to 2 per cent. of hydrochloric acid as before.

100 parts of grape sugar, found by Fehling's process, represent 90 parts of starch or dextrin. When dextrin is present with grape sugar, care must be taken not to boil the mixture too long with the alkaline copper solution, as it has been found that a small portion of the copper is precipitated by the dextrin.‡

The hydrolysis of starch may be brought about more rapidly, and at lower temperature, by using some form of diastase in place of acid. An infusion of malt is best suited to the purpose,

* *Chem. Zeit.* 1895, **19**, 1501. † *Chem. Centralbl.* **8**, 732.

‡ Rumpf and Heintzerling, *Z. a. C.* **9**, 358.

but the temperature must not exceed 71° C. (160° Fahr.). The digestion may vary from fifteen minutes to as many hours. The presence of unchanged starch may be ascertained by occasionally testing with iodine. If the digestion is carried beyond half an hour, a like quantity of the same malt solution must be digested alone, at the same temperature and for the same time, then titrated for its amount of sugar, which is deducted from the total quantity found in the mixture. O'Sullivan* has, however, clearly shown that the effect of the diastase is to produce maltose, which has only the power of reducing the copper solution to the extent of about three-fifths that of dextrose or grape sugar, the rest being probably various grades of dextrin. Brown and Heron's experiments clearly demonstrate that no dextrose is produced from starch by even prolonged treatment with malt extract; the only product is maltose. Sulphuric or other similar acids cause complete hydrolysis.

For the exact determination of starch in grain of various kinds O'Sullivan gives very elaborate directions, involving the treatment of the substance with alcohol and ether, to remove fatty and other constituents previous to digestion with diastase. The same authority also gives special directions for the preparation of the proper kind of diastase, all of which may be found in *J. C. S.* xlv. 1.

For a rapid determination of starch in barley or malt a method has been described by H. T. Brown and J. H. Millar.†

Preparation of the Solution of Sugar.—For all the processes of titration this must be so diluted as to contain ½ or at most 1 per cent. of sugar; if on trial it is found to be stronger than this, it must be further diluted with a measured quantity of distilled water.

If the sugar solution to be examined is of dark colour, or likely to contain extractive matters which might interfere with the distinct ending of the reaction, it is advisable to heat a measured quantity to boiling, and add a few drops of milk of lime, allow the precipitate to settle, then filter through purified animal charcoal, and dilute with the washings to a definite volume. In some instances cream of alumina or basic lead acetate may be used to clarify highly coloured or impure solution, but no lead must be left in the solution.‡

From thick mucilaginous liquids, or those which contain a large proportion of albuminous or extractive matters, the sugar is best extracted by Graham's dialyzer.

* *J. C. S.* 1872, 579. † *Trans. of the Guinness Research Lab.* 1903, 1, 79.

‡ Although traces of lead are of no great consequence when clarifying sugars for the polarimeter it is of great importance to remove all lead when using the volumetric method. In order to do this it is best to treat a measured quantity of the sugar solution which has been clarified by lead with a strong solution of sulphurous acid until no further precipitate is formed, then add a few drops of aluminium hydrate suspended in water, dilute to a definite volume and filter. In many cases concentrated solution of sodium carbonate will suffice to remove all lead. These methods of clarification are highly necessary in the case of albuminous or gelatinous liquids, as otherwise the copper oxide will not settle readily, and it becomes difficult to tell when the end-reaction occurs.

The Fehling method may be applied directly to fresh diabetic urine (see Analysis of Urine), as also to brewer's wort or distiller's mash. Dextrin does not interfere, unless the boiling of the liquid under titration is long continued.

2. Determination of Glucose by Fehling's Solution.

Preparation of the Standard Solutions.—Fehling's standard copper solution.—Crystals of pure cupric sulphate are powdered and pressed between unsized paper to remove adhering moisture; 69·28 gm. are weighed, dissolved in water, about 1 c.c. of pure sulphuric acid added, and the solution diluted to 1 litre.

Alkaline tartrate solution.—350 gm. of Rochelle salt (sodium potassium tartrate) are dissolved in about 700 c.c. of water, and the solution filtered, if not already clear; there is then added to it a clear solution of 100 gm. of caustic soda (prepared by alcohol) in about 200 c.c. of water. The volume is made up to 1 litre at 60° Fah.

These solutions are prepared separately, and when mixed in exactly equal proportions form the original Fehling solution, each c.c. of which should contain 0·03464 gm. of cupric sulphate, and represents 0·005 gm. of pure anhydrous grape sugar, if the conditions of titration laid down below are adhered to.* The method is based on the fact that although Fehling's solution may be heated to boiling without change, the introduction into it of the smallest quantity of grape sugar, at a boiling temperature, at once produces a precipitate of cuprous oxide, the ratio of reduction being uniform if the conditions of experiment are always the same.

THE TITRATION OF GLUCOSE WITH FEHLING'S SOLUTION.—5 c.c. each of standard copper and alkaline tartrate solutions are accurately measured into a thin white porcelain basin, 40 c.c. of water added, and the basin quickly heated to boiling on a sand-bath or by a small flame. No reduction or change of colour should occur; if it does, the alkaline tartrate solution is probably defective from age. This may probably be remedied by the addition of a little fresh caustic alkali on second trial, but it is advisable to use a new solution. The ½ or 1 per cent. sugar solution is then delivered in from a burette† in small quantities at a time, with subsequent boiling, until the blue colour of the copper solution is just discharged, a point which is readily detected by inclining the basin, so that the colour of the clear supernatant fluid may be observed against the white sides of the basin. Some operators use a small thin boiling flask instead of the basin.

It is almost impossible to hit the exact point of reduction in the first titration, but it affords a very good guide for a more rapid

* If pure cupric sulphate has been used, and the solutions mixed only at the time of titration, there need be very little fear of inaccuracy; nevertheless it is advisable to verify the mixed solutions from time to time. This may be done by weighing and dissolving 0·95 gm. of pure cane sugar in about 50 c.c. of water, adding 2 c.c. of hydrochloric acid, and heating to 70° C. for ten minutes. The acid is then neutralized with sodium carbonate and diluted to a litre. 50 c.c. of this liquid should exactly reduce the copper in 10 c.c. of Fehling's solution. A standard solution of invert sugar, which will keep good for many months, may be made in the foregoing manner; it should be of about 20 per cent. strength, and rendered strongly alkaline with soda or potash.

† The instrument should be arranged as described on page 12.

and exact addition of the sugar solution in a second trial, when the sugar may be added with more boldness, and the time of exposure of the copper solution to the air lessened, which is a matter of great importance, since prolonged boiling has undoubtedly a prejudicial effect on the accuracy of the process.

The volumetric determination of reducing sugars is dealt with by A. R. Ling and T. Rendle,* and by A. R. Ling and G. C. Jones,† who describe a modification of the volumetric method, by which results are obtained equal in accuracy to those of the gravimetric method of Brown, Morris and Millar.‡ The average error is 1 in 300. The principal points in this method are that the titration is performed in a boiling flask on 10 c.c. of *undiluted* Fehling's solution, and that ferrous thiocyanate is used as indicator.

The indicator is prepared by dissolving ammonium thiocyanate (1·5 grams), ferrous ammonium sulphate (1 gram), in concentrated hydrochloric acid (2·5 c.c.) and water (10 c.c.). The solution so obtained has invariably a red colour, due to the presence of ferric salt which is readily reduced by addition of a trace of zinc dust. The indicator when kept for some hours develops the red coloration by atmospheric oxidation and must again be reduced. In practice it is found that the freshly prepared indicator is too sensitive, and that it is most useful after it has been reduced twice with zinc dust. The method of titration is as follows:—Freshly mixed Fehling's solution (10 c.c.) is accurately measured into a 200 c.c. boiling flask and raised to boiling. The sugar solution, which should be adjusted to such a strength that 20 to 30 c.c. of it are required to reduce 10 c.c. of Fehling's solution, is then run into the boiling liquid in small amounts, commencing with 5 c.c. After each addition of sugar solution, the mixture is boiled, the liquid being kept rotated. About a dozen drops of the indicator are placed on a porcelain or opal glass slab, and when it is judged that the precipitation of cuprous oxide is complete, a drop of the liquid is withdrawn by a clean glass rod or by a capillary tube, and brought in contact with a drop of the indicator on the slab. The test must be carried out rapidly. It is also essential to perform the titration as rapidly as possible, as an atmosphere of steam is then kept in the neck of the flask, and the influence of atmospheric oxygen avoided. At the final point, the liquid is boiled for about ten seconds. Duplicate titrations should agree to 0·1 c.c. The only defect of this indicator is that it cannot be used with products containing ferric iron. The titration can be carried out by artificial light.

To standardize Fehling's solution, Ling and Rendle (*loc. cit.*) dissolve pure sucrose (0·95 gram) in water (150 c.c.), and boil for one minute with $^N/_2$ hydrochloric acid (30 c.c.). After cooling the solution is neutralized with $^N/_2$ sodium hydroxide (30 c.c.) and made up to 500 c.c. It is then titrated as above against 10 c.c. of Fehling's solution. The relative amounts of anhydrous invert sugar, dextrose, and maltose required to reduce a fixed volume of Fehling's solution are 100 : 96 : 161 ; but in the case of the first two sugars the ratio varies somewhat with concentration. Ling and Jones|| give a table to correct for this. It may be required in the analysis of commercial invert sugar when the percentage of dextrose and of laevulose are separately reported.

A method has been proposed for indicating when all copper has been precipitated by E. F. Harrison,§ and is very sensitive. It depends upon the action of copper salts in liberating iodine from iodide.

* *Analyst*, 1905, **30**, 182; 1908, **33**, 167. † *Ibid*, 1908, **33**, 160.

‡ *J. Chem. Soc. Trans.*, 1897, 71, 112. || (*loc. cit.*, 165).

§ *Pharm. Journ.* 1903, 170.

The indicator is prepared by boiling 0·05 gm. of starch with a few c.c. of water, adding 10 gm. of potassium iodide and diluting to 100 c.c. These quantities need not of course be exactly adhered to, but too much starch or too little iodide lessens the delicacy of the test; the solution should be prepared as required, and not used after it has been made more than two or three hours. In use about 0·5 or 1 c.c. of this solution is taken, acidified with about five or ten drops of acetic acid, and one drop or more of the titration liquid added; the latter need not be filtered. As long as unreduced copper is present, a colour is produced, varying from red to blue, and of greater or less intensity, according as the end-point is far off or near. The production of no colour marks the end of the reaction.

This indicator gives a readily observed colour with one drop of a solution of copper sulphate of strength 1 in 20,000, and by its use titration of Fehling's solution with a suitable sugar solution can be made as accurate as most other volumetric operations. After very little practice one titration is sufficient for moderately accurate results, but greater exactness is of course obtained by repeating, and at once running in the sugar solution almost up to the required amount before testing.

When the exact point of reduction is obtained, it is assumed that the volume of sugar solution used represents 0·05 gm. of grape sugar or glucose, for 10 c.c. Fehling's solution contain 0·11 gm. cupric oxide, and 5 molecules CuO (397·85) are reduced to cuprous oxide by 1 molecule of glucose (180·1), therefore 397·85 : 0·11 = 180·1 : 0·05 *i.e.*, 0·05 gm. glucose exactly reduces 10 c.c. Fehling's solution.

With this assumption, however, Soxhlet does not agree, but maintains from the results of his experiments on carefully prepared standard sugars that the accuracy of the reaction is interfered with by varying concentration of the solutions, duration of the experiment, and the character of the sugar.

For example, he found that the reducing power of glucose, invert sugar, and galactose was in each case lowered by dilution of the Fehling's solution, whilst that of maltose was raised, and that of milk sugar was not affected.

The remarks which Soxhlet appends to his experiments are thus classified:—

(1) The reducing power of invert sugar for alkaline copper solution is greatly influenced by the concentration of the solutions: a smaller quantity of sugar being required to decompose Fehling's solution in the undiluted state than when it is diluted with 1, 2, 3, or 4 volumes of water. It is immaterial whether the sugar solution be added to the cold or boiling copper reagent.

(2) If invert sugar acts on a larger quantity of copper solution than it is just able to reduce, its reducing power will be increased, the increment varying according to the amount of copper in excess and the concentration of the cupric liquid; in the previous experiments the equivalents varied from 1 : 9·7 to 1 : 12·6, these numbers being by no means the limit of possible variation.

(3) In a volumetric determination of invert sugar by means of Fehling's solution, the amount of copper reduced by each successive addition of sugar solution is a decreasing quantity; the results obtained are therefore perfectly empirical, and are only true of that particular set of conditions.

(4) The statement that 1 equivalent of invert sugar reduces 10 equivalents of cupric oxide is not true, the hypothesis that 0·5 gm. invert sugar reduces 100 c.c. of Fehling's solution being shown to be incorrect; the real amount under the conditions laid down by Fehling (1 volume of alkaline copper solution, 4 volumes of water, sugar solution ½-1 per cent.) being 97 c.c. the results obtained under this hypothesis are, therefore, 3 per cent. too low. Where, however, the above conditions have been fulfilled, the results, although not absolutely, are relatively correct; not so, however, those obtained by gravimetric

processes, since the interference of concentration and excess has not been previously recognized.

These facts, however, do not vitiate the process as carried out under the well recognized conditions insisted on in the directions for titration that were given above. If these are adhered to it is found that the sugars have the following reducing powers—

10 c.c. Fehling's solution are completely reduced by

0·05 gm. glucose, laevulose, galactose
0·0475 gm. cane sugar (after hydrolysis)
0·0678 gm. milk sugar
0·0807 gm. maltose
0·045 gm. starch (after hydrolysis).

Lowe and, more recently, Haines have advocated the substitution of an alkaline solution of glycerine for the alkaline tartrate in Fehling's solution. This solution is said to keep indefinitely, but it is not so delicate a test as Fehling's.

Determination of the Cuprous Oxide by Permanganate.—In cases where it is permissible to weigh the cuprous oxide produced in the Fehling method, R. M. Caven and A. Hill* have devised a volumetric method by which the amount precipitated can be determined in a shorter time, and with very fair accuracy.

The necessary standard solutions are potassium permanganate about $^N/_5$ strength, the exact oxygen value of which is known, and an oxalic acid solution of preferably the same strength. These must be titrated together in the same way as in the actual process.

There is also required a dilute sulphuric acid, 1 of acid to 3 of water.

Method of Procedure: The cuprous oxide, whether from a sugar determination or other sources, is best collected on an asbestos filter connected with water pump as follows:—Selected fibrous asbestos is cut into pieces an eighth of an inch in length, digested with strong sulphuric acid to destroy organic matter, then thoroughly washed, and mixed into a paste with water. For the preparation of the filter it is best to use a Hirsch's porcelain funnel with perforated filter plate; pouring the asbestos cream into the funnel, and applying suction by means of the filter pump until a mat of asbestos, suitable to receive the precipitated cuprous oxide, is obtained. After the removal of the beaker containing the precipitated cuprous oxide from the water-bath, the supernatant liquid is at once decanted through the filter, and the cuprous oxide remaining in the beaker is stirred up with hot water, transferred to the filter, and washed until free from alkali. The last traces of cuprous oxide need not be removed from the beaker, as these can be dissolved later on in a little of the acidified permanganate solution. The asbestos containing the cuprous oxide is transferred by means of a glass rod to a porcelain dish about eight inches in diameter, and the mass thoroughly broken up with water.

If the quantity of oxide does not exceed 0·2 gm., 20 or 25 c.c. of the standard permanganate are mixed with 80 or 100 c.c. of the dilute sulphuric acid and poured over the cuprous oxide, and the mixture well stirred till dissolved. Boiling water is then added so as to bring the temperature to 45° or 50° C., but not more than the latter. It is now ready for titration. It is found best to add excess of oxalic acid solution, after adjusting the temperature of the liquid, and then to titrate back with the permanganate. This process is very rapid, owing to the use of the filter pump, and it gives consistent and good results.

* *J. S. C. I.* **16**, 981 and **17**, 124.

The amount of cuprous oxide corresponding to the volume of permanganate used, is calculated by multiplying the oxygen value of the number of c.c. used by the factor 8·946 $\left(=\frac{Cu_2O}{O}\right)$. The authors use the factor 0·5045 for the conversion of weight of Cu_2O into dextrose, laevulose, or invert sugar. The most important application of this process is its use in the analysis of sugars by the determination of their cupric reducing power. For this purpose the hot solution of sugar is introduced into excess of Fehling's solution contained in a beaker immersed in the water-bath, and the reduction allowed to proceed for 14 minutes, according to the method recommended by C. O'Sullivan (Watts's Dict., art. Sugar). The method can of course be used for the determination of copper as cuprous oxide in cases other than sugar analysis.

The cuprous iodide process may be also used to ascertain the amount of copper not precipitated by the sugar. Several operators have experimented on the method, the best form of which is that given by Schoorl.* Results agreeing with the gravimetric determinations can be obtained if a fair excess of potassium iodide be used, and if this be added to the alkaline liquid prior to acidification. The author describes the following modification as being convenient.

METHOD OF PROCEDURE: 10 c.c. of Fehling's copper solution (10 c.c. = 27·75 c.c. $^{N}/_{10}$ thiosulphate) are mixed with 10 c.c. of Soxhlet's alkaline tartrate solution in an Erlenmeyer flask of 200 c.c. capacity. Water is added to make up 50 c.c. and the contents of the flask are boiled for 2 minutes on wire gauze, over which is placed an asbestos ring having a hole 6 cm. in diameter. The liquid is then quickly and thoroughly cooled under the tap, and 10 c.c. of a 20 per cent. solution of potassium iodide with 10 c.c. of 25 per cent. sulphuric acid (1·5 of concentrated acid with 8·5 of water by volume) are added. The iodine liberated is immediately titrated with decinormal thiosulphate with the addition of starch until the blue colour changes to cream. After this blank experiment, a similar one in every respect is made, introducing a known quantity of sugar solution in place of some of the water making up to 50 c.c. Not more than 90 mgm. of glucose or invert sugar or 125 mgm. of lactose should be taken, and in the determination of lactose, the liquids should be boiled for 5 minutes instead of 2. When the sugar is impure care should be taken to determine whether there is any impurity capable of combining with iodine.

T. B. Wood and R. A. Berry† have devised the following method for use where a polarimetric determination is not possible.

The saccharine solution is clarified by means of basic lead acetate, the cane sugar present inverted by treatment with dilute acid, the solution neutralized and diluted till it contains from 0·5 to 1·0 per cent. of reducing sugar. 10 c.c. of the sugar solution are now added to 50 c.c. of a boiling copper solution (23·5 gm. of copper sulphate, 250 gm. of potassium carbonate and 100 gm. of potassium bicarbonate per litre) and the mixture boiled for 10 minutes. The cuprous oxide precipitated is filtered off in a Gooch crucible, washed with boiling water, and transferred to a flask filled with carbon dioxide. It is then shaken vigorously for a few moments with 25 c.c. of 2½ per cent. solution of ferric sulphate in 25 per cent. sulphuric acid, whereby the cuprous oxide dissolves, reducing an equivalent amount of ferric sulphate to the ferrous salt. The latter is titrated with a solution of potassium permanganate of such strength that 1 c.c. is equivalent to 0·01 gm. of copper.

* *Zeit. angew Chem.* 1899, 633.

† Proc. Cambridge Phil. Soc., 1903, 12, 97-98.

3. Determination of Glucose by Mercury.

Knapp's Standard Mercuric cyanide.—10 gm. of pure dry mercuric cyanide are dissolved in about 600 c.c. of water; 100 c.c. of caustic solution (sp. gr. 1·145) are added, and the liquid diluted to 1 litre.

Sachsse's Standard Mercuric iodide.—18 gm. of pure dry mercuric iodide and 25 gm. of potassium iodide are dissolved in water, and to the liquid is added a solution of 80 gm. of caustic potash; the mixture is finally diluted to 1 litre.

These solutions, if well preserved, will hold their strength unaltered for a long period.

These solutions are very nearly, but not quite, the same in mercurial strength, Knapp's containing 7·9365 gm. Hg in the litre, Sachsse's 7·9295 gm. 100 c.c. of the former are equal to 100·1 c.c. of the latter.

Indicators for the Mercurial Solutions.—In the case of Fehling's solution, the absence of blue colour acts as a sufficient indicator, but with mercury solutions the end of reaction must be found by an external indicator. In the case of Knapp's solution the end of the reaction is found by placing a drop of the clear yellowish liquid above the precipitate on pure white Swedish filter paper, then holding it first over a bottle of fuming HCl, then over strong sulphuretted hydrogen water; the slightest trace of free mercury shows a light brown or yellowish-brown stain. The indicator best adapted for Sachsse's solution is a strongly alkaline solution of stannous chloride spotted on a porcelain tile. An excess of mercury gives a brown colour.

Method of Procedure: 40 c.c. of either solution are placed in a porcelain basin or a flask, diluted with an equal bulk of water, and heated to boiling. The solution of sugar of ½ per cent. strength is then delivered in until all the mercury is precipitated, theory indicating that in either case 40 c.c. should be reduced by 0·1 gm. of dextrose.

The results of Soxhlet's experiments show that this estimate is entirely wrong*; nevertheless, it does not follow that these mercurial solutions are useless. It is found that, using them by comparison with Fehling's solution, it is possible to define to some extent the nature of mixed sugars, on the principle of indirect analysis.

Knapp's solution is strongly recommended by good authorities for the determination of diabetic sugar in urine. The method of using it is described in the section on Urinary Analysis.

The behaviour of the sugars with alkaline mercury solutions was tested by Soxhlet both with Knapp's solution and Sachsse's solution.

He found that different results are obtained from Knapp's solutions, according as the sugar solution is added gradually or all at once; when gradually added more sugar is required; with Sachsse's, however, the reverse is the case.

* Careful experiment shows that 40 c.c. of Sachsse's solution is reduced by 0·1342 gm. dextrose or 0·1072 gm. invert sugar.

To get comparable results the sugar must be added all at once, the solution boiled for two or three minutes, and the liquid tested for mercury, always using the same indicator; in using the alkaline tin solution as indicator, 0·200-0·202 gm. of grape sugar was always required for 100 c.c. Knapp, this being proved by a large number of experiments. It is remarkable that these two solutions, although containing almost exactly the same amount of mercury, require very different quantities of sugar to reduce equal volumes of them. This is shown to be due, to a great extent, to the different amounts of alkali present in them.

The various sugars have different reducing powers for the alkaline mercury solutions, and there is no definite relation between the amount of Knapp's and Sachsse's solutions required by them; the amount of Sachsse's solution, to which 100 c.c. Knapp's correspond, varying from 54·7 c.c. in the case of galactose to 74·8 in the case of invert sugar.

The two mercury methods have no advantage in point of accuracy or convenience over Fehling's method, the latter having the preference on account of the great certainty of the point at which the reduction is finished.

The mercury methods are, however, of great importance, both for the identification of a sugar and for the determination of two sugars in presence of each other, as proposed by Sachsse. For instance, in the determination of grape and invert sugars in presence of each other there are the two equations: $ax+by=F$, $cx+dy=S$.

Where—

a = number of c.c. Fehling reduced by 1 gm. grape sugar.
b = ,, ,, ,, ,, invert sugar.
c = ,, Sachsse ,, ,, grape sugar.
d = ,, ,, ,, ,, invert sugar.
F = ,, Fehling used for 1 vol. sugar solution.
S = ,, Sachsse ,, ,, ,,
x = amount of grape sugar in gms. in 1 vol. of the solution.
y = ,, invert sugar ,, ,, ,,

It need hardly be mentioned that the above, like all other indirect methods, leaves room for increased accuracy; but nevertheless the combination of a mercury method with a copper method, in the determination of a sugar whose nature is not exactly knows, gives a more serviceable result than the hitherto adopted plan, by which a solution that reduced 10 c.c. Fehling was said to contain 0·05 gm. of sugar.*

Taking the reducing power of grape sugar = 100, the reducing powers of the other sugars are:—

	Fehling (undiluted).	Knapp.	Sachsse.
Grape Sugar	100	100	100
Invert sugar	96·2	99·0	124·5
Laevulose (calculated) ..	92·4	102·2	148·6
Milk sugar	70·3	64·9	70·9
Galactose	93·2	83·0	74·8
Hydrolyzed milk sugar	96·2	90·0	85·5
Maltose	61·0	63·8	65·0

* *J. C. S.* Abstracts, 1880, 758.

4. Sidersky's Method.

This process has found great favour among French sugar experts, and is based on the use of Soldaini's cupric solution, which was devised to remedy the faults common to Fehling's and other copper solutions containing tartrated and caustic or carbonated alkalies.

This liquid is prepared, according to Degener, in the following manner :—40 gm. of cupric sulphate are dissolved in water, and, in another vessel, 40 gm. of sodium carbonate are also dissolved in water. The two solutions are mixed, and the copper precipitated in the state of hydrated basic carbonate. The precipitate is washed with cold water and dried. This precipitate is added to a very concentrated and boiling solution of potassium bicarbonate (about 415 gm.) and agitated until the whole is completely or nearly dissolved, water is added to make up the volume to 1400 c.c., and the whole mass heated for two hours upon a water-bath. The insoluble matter is filtered off, and the filtrate, after cooling, is of a deep blue colour. The sensibility of this liquid is so great that it gives a decided reaction with 0·0014 gm. of invert sugar. The presence of sucrose in the solution increases this sensibility still more.

Sidersky has recently offered a new volumetric method, based upon the use of Soldaini's solution. With sugars the same method as is now in use with Fehling's solution can easily be followed, watching the disappearance of the blue colour, and testing the end with ferrocyanide and acetic acid. This process offers no serious objections common to Fehling's solution, but is inapplicable to coloured sugar solutions, such as molasses, etc. For the last the following is recommended :—

METHOD OF PROCEDURE : 25 gm. of molasses are dissolved in 100 c.c. of water and subacetate of lead added in sufficient quantities to precipitate the impurities, and the volume raised to 200 c.c. and filtered. To 100 c.c. of the filtrate are added 25 c.c. of concentrated solution of sodium carbonate, agitated, and filtered again. 100 c.c. of the second filtrate with excess of lead removed are taken for analysis. On the other hand, 100 c.c. of Soldaini's solution are placed in a flask and heated five minutes over an open flame. The sugar solution is now added little by little, and the heating continued for five minutes. Finally, the heat is withdrawn and cooled by turning in 100 c.c. of cold water, and filtered through a Swedish filter, washed with hot water, letting each washing run off before another addition. Three or four washings will generally remove completely the alkaline reaction. The precipitate is then washed through a hole in the filter into a flask, removing the last trace of copper. 25 c.c. of normal sulphuric acid are added with two or three crystals of potassium chlorate, and the whole gently heated to dissolve completely the oxide of copper, which is transformed into copper sulphate. The excess of sulphuric acid is determined by a standard ammonia solution (semi-normal) of which the best indicator is the sulphate of copper itself. When the deep blue colour gives place to a greenish tinge the titration is completed. The method of titration is performed as follows :—Having cooled the contents of the flask, a quantity of ammonia equivalent to 25 c.c. of normal sulphuric acid is added. From a burette graduated into one-tenth c.c. standard sulphuric acid is dropped in drop by drop, agitating after each addition. The blue colour disappears with each addition, to reappear after shaking. When the last trace of ammonia is saturated the titration is complete, which is known by a very feeble greenish tinge. The number of c.c. is read from the burette, which is equivalent to the copper precipitated. The equivalent of copper being taken at 31·78, the normal acid equivalent is 0·03178

of copper. Multiplying the copper found by 3546 the invert sugar is found. A blank titration is needed to accurately determine the slight excess which gives the pale green tinge.*

5. Pavy's modified Fehling Process.

This method consists in adding ammonia to the ordinary Fehling solution, by which means the precipitation of cuprous oxide is entirely prevented, the end of the reaction being shown by the disappearance of the blue colour in a perfectly clear solution.†

The solution recommended by Pavy is made by mixing 120 c.c. ordinary Fehling solution‡ (see page 327) with 300 c.c. of strong ammonia (sp. gr. 0·880), adding 100 c.c. of a 10 per cent. caustic soda solution or of a 14 per cent. solution of potash, and diluting to a litre. If Fehling's solution is not available, Pavy's solution may be made directly by adding a cooled solution of 21·6 gm. Rochelle salt and 18·4 gm. of soda (or 25·8 gm. of potash) to a solution of 4·157 gm. pure cupric sulphate, adding 300 c.c. of strong ammonia and making up to a litre. 100 c.c. Pavy's solution =10 c.c. Fehling's solution=0·05 gm. of glucose.

As ammoniacal cuprous solutions are readily oxidized, it is important to exclude air from the liquid during titration. The titration should be made in a small boiling flask, through the cork of which the elongated end of the burette is passed. A small escape tube, preferably with a valve, also passes through the same cork, and leads into a vessel containing water or weak acid, to condense the ammonia. Allen has found a layer of paraffin over the liquid an effective means of excluding air.

In carrying out the titration (100 c.c. of the Pavy's solution is a convenient quantity to take) a few pieces of pumice or pipe-stem are added, the liquid brought to boiling, and kept boiling whilst the sugar solution is gradually run in. The end-point is very sharp. Whilst rapid manipulation is desirable, the solution must not be run in too quickly, because reduction takes place more slowly than with Fehling's solution.

The method is well adapted for the examination of diabetic urine and milk, also mixtures of milk and cane sugars, and certainly has the advantage over the ordinary Fehling method by its definite end point.

Z. Peska|| gives the following method for the volumetric determination of sugar by means of ammoniacal copper solution. In order to avoid the oxidation of the copper oxide in solution, a layer of vaseline is used instead of the usual current of hydrogen. Two solutions are prepared : 6·927 gm. of the purest crystallized copper sulphate are dissolved in water, 160 c.c. of 25 per cent, ammonia added, and the whole made up to 500 c.c. ; 34·5 gm. of Rochelle

* Report of Proceedings of Fifth Annual Convention of the American Association of Official Agricultural Chemists (1888). † *C. N.* **40**, 77.

‡ In ammoniacal solution only 5 molecules CuO are reduced by 1 molecule glucose instead of 6 CuO, as in Fehling's solution, hence 120 c.c. of the latter are used in making Pavy's solution and not 100 c.c. || *Chem Zeit. Rep.* 1895, 257.

salt and 10 gm. of caustic soda are also dissolved and diluted to 500 c.c.

METHOD OF PROCEDURE: A mixture of 50 c.c. of each liquid is heated in a beaker under a layer of vaseline oil 5 mm. thick, to a temperature of 80° C. The sugar solution is run in 1 c.c. at a time for the first test, but on a repetition the whole amount may be added at once. Towards the end of the titration, the temperature must be raised to 85°, and the heating continued for two minutes when working on either glucose or invert sugar, four minutes for maltose, and six minutes for milk sugar. Dextrin increases the reducing power of the sugar in this solution less than in the one prepared with potash, and as the ammonia has no injurious action, the whole process is both exact and convenient. When sucrose is present, 1 gm. of it has a reducing action equivalent to 0·026 gm. of invert sugar. In the determination of lactose in milk the albuminoids should be precipitated with lead acetate and the excess of lead removed by sodium sulphate. The following table gives directly the number of milligrams of each sugar in 100 c.c. of solution.

c.c. used.	Glucose.	Invert sugar.	Milk sugar.	Maltose.	c.c used.	Glucose.	Invert sugar.	Milk sugar.	Maltose.
8	997·8	1049·2	—	—	50	163·0	173·2	318·1	360·0
9	889·4	935·1	—	—	51	159·8	169·8	311·9	353·0
10	802·3	844·6	—	—	52	156·8	166·5	306·0	346·3
11	730·7	770·0	—	—	53	153·9	163·4	300·3	339·9
12	670·8	707·6	—	—	54	151·1	160·4	294·8	333·8
13	620·0	654·5	—	—	55	148·4	157·5	289·4	327·9
14	576·3	608·7	—	—	56	145·7	154·7	284·2	322·2
15	538·4	568·9	1033·9	—	57	143·1	152·0	279·3	316·7
16	505·2	534·2	971·4	—	58	140·6	149·4	274·5	311·4
17	475·8	503·3	916·0	1023·0	59	138·2	146·9	269·9	306·3
18	449·7	475·7	866·5	968·8	60	135·9	144·5	265·4	301·3
19	426·3	451·2	822·3	920·3	61	133·7	142·2	261·1	296·4
20	405·2	429·0	782·4	876·3	62	131·5	139·9	256·9	291·6
21	386·0	408·8	746·0	836·4	63	129·4	137·7	252·9	287·0
22	368·7	390·6	713·0	800·0	64	127·4	135·5	249·0	282·6
23	352·8	373·8	682·7	766·5	65	125·4	133·4	245·2	278·3
24	338·2	358·4	654·8	735·8	66	123·5	131·4	241·5	274·1
25	324·8	344·3	629·2	707·5	67	121·7	129·5	237·9	270·0
26	312·4	331·2	605·5	681·3	68	119·9	127·6	234·4	266·1
27	300·9	319·3	583·5	656·8	69	118·2	125·7	231·0	262·3
28	290·3	307·8	563·1	634·1	70	116·5	123·9	227·7	258·6
29	280·3	297·3	544·1	613·0	71	114·9	122·2	224·6	255·0
30	271·1	287·5	526·2	593·2	72	113·3	120·5	221·5	251·5
31	262·4	278·2	509·5	574·5	73	111·8	118·9	218·5	248·1
32	254·2	269·6	493·8	557·1	74	110·3	117·3	215·6	244·8
33	246·6	261·6	479·1	540·8	75	108·8	115·8	212·8	241·6
34	239·3	253·9	465·3	525·3	76	107·4	114·3	210·0	238·4
35	232·6	246·7	452·2	510·7	77	106·0	112·8	207·3	235·3
36	226·1	240·0	439·8	496·8	78	104·6	111·4	204·7	232·3
37	220·0	233·5	428·1	483·7	79	103·3	110·0	202·1	229·4
38	214·3	227·4	417·0	471·3	80	102·0	108·6	199·6	226·6
39	208·8	221·7	406·5	459·5	81	100·8	107·2	—	223·9
40	203·6	216·2	396·5	448·3	82	99·6	105·9	—	221·2
41	198·7	211·0	387·0	437·6	83	—	104·6	—	218·6
42	194·1	206·0	377·8	427·4	84	—	103·4	—	216·0
43	189·7	201·3	369·2	417·7	85	—	102·2	—	213·5
44	185·4	196·7	360·9	408·4	86	—	101·1	—	211·1
45	181·2	192·3	353·0	399·5	87	—	—	—	208·7
46	177·3	188·1	345·4	391·0	88	—	—	—	206·4
47	173·5	184·1	338·1	382·8	89	—	—	—	204·1
48	169·9	180·3	331·2	374·9	90	—	—	—	201·9
49	166·4	176·7	324·5	367·3	91	—	—	—	199·7

6. Gerrard's Cyano-cupric Process.

This process, as improved by Gerrard* and A. H. Allen, has proved a valuable addition to the processes of titration based on the reducing power of glucose. It has the advantage over Pavy's method in causing no evolution of ammonia ; moreover, the reduced solution is reoxidized so slowly that titration may with reasonable expedition even be conducted in an open dish. The process is based on the following facts :—When a solution of potassium cyanide is added to a solution of copper sulphate a colourless stable double cyanide of copper and potassium is formed, thus :—

$$CuSO_4 + 4KCy = CuCy_2, 2KCy + K_2SO_4.$$

This salt is not decomposed by alkalies, hydrogen sulphide, or ammonium sulphide. If potassium cyanide be added to Fehling's solution the latter is decolourized, the above double salt being formed at the same time, and if the colourless solution be boiled with glucose no cuprous oxide is precipitated. If there be present excess of Fehling's solution over the amount capable of being decolorized by the potassium cyanide, the mixture is blue, and when it is boiled with a reducing sugar the extra portion is reduced, but no cuprous oxide is precipitated, the progress of the reduction being marked by the gradual and final disappearance of the colour of the solution, just as in Pavy's process.

Process of Titration : 10 c.c. of freshly made Fehling's solution, or 5 c.c. of each of the constituent solutions, are diluted with 40 c.c. of water in a porcelain dish and heated to boiling. An approximately 5 per cent. solution of potassium cyanide is added very cautiously from a burette or pipette to the still boiling and well agitated blue liquid till the colour is just about to disappear. Excess of cyanide must be carefully avoided.†

10 c.c. of Fehling's solution are now accurately measured into the dish, and the sugar solution (of about ½ per cent. strength glucose) run in slowly from a burette, with constant stirring and ebullition, till the blue colour disappears. Only the second measure of Fehling's solution suffers reduction. The volume of sugar solution run in contains 0·05 gm. of glucose.

Some technical applications of the Solutions to mixtures of various Sugars.

It cannot be claimed for these determinations that they are absolutely exact ; but with care and practice, accompanied with uniform conditions, they are probably capable of the best possible results whatever methods may be used.

Cane-Sugar, Grape-Sugar, and Dextrin.‡ The solution containing these three forms is first titrated with the usual Fehling solution for grape sugar. A second portion is boiled with acetic acid (which only inverts cane sugar) and titrated. Finally, a third portion is completely hydrolyzed with sulphuric acid and titrated.

* *Year Book Pharm.* 1892, 400.

† As the double cyanide solution keeps for some time, a stock may be made up, so that 50 c.c. contain 10 c.c. of Fehling's solution, and that volume taken for each titration, instead of going through the process of exact decolourization every time.

‡ *Biard & Pellett, Z. a. C.* **24**, 275

The difference between the first and second titrations gives the cane sugar, and that between the second and third the dextrin.

Another method might be suggested as follows :—First determine the grape-sugar by Fehling's solution. Next, convert the sucrose into invert-sugar by the action of invertase—the other constituents being unaffected—and determine the grape- and invert-sugars together by a second titration with Fehling. Finally, the solution is heated for some hours with dilute sulphuric acid, whereby the cane-sugar is inverted and the dextrin hydrolyzed to dextrose : the solution is then titrated for the third time. The difference between the third and second titrations gives the dextrose-equivalent of the dextrin present. (Or the dextrin may be determined gravimetrically by pouring the aqueous solution into a large excess of rectified spirit in a weighed beaker. After standing till the precipitate is completely settled the liquid is poured off, and the dextrin weighed).

Milk-Sugar and Cane-Sugar.—If the determination of milk sugar is alone required, and by the usual Fehling solution, the casein and albumen must first be removed. Acidify the liquid with a few drops of acetic acid, warm until coagulation is effected, and filter. Boil the filtrate to coagulate the albumen. Filter again, and neutralize with soda previous to treatment for sugar by the copper test. The number of c.c. of Fehling's solution required, multiplied by 0·006786, will give the weight of milk sugar in grams. Direct determination by Pavy-Fehling is preferable to this method. Cane sugar in presence of milk sugar may be determined as follows :—Dilute the milk to ten times its bulk, having previously coagulated it with a little citric acid, filter, and make up to a definite volume, titrate a portion with Pavy-Fehling solution, and note the result. Then take 100 c.c. of the filtrate, add 2 gm. of citric acid, and boil for 10 minutes, cool, neutralize, make up to 200 c.c., and titrate with copper solution as before. The difference between the reducing powers of the solutions before and after inversion is due to the cane sugar, the milk sugar not being affected by citric acid.

Stokes and Bodmer* have experimented largely on this method, and with satisfactory results. The plan adopted by them is to use 40 c.c. of Pavy-Fehling liquid (=0·02 gm. glucose), and to dilute the sugar solution (without previous coagulation), so that from 6 to 12 c.c. are required for reduction. By using a screw-clamp on the rubber burette tube, the sugar solution is allowed to drop into the boiling liquid at a moderate rate. If Cu_2O should be precipitated before the colour disappears, a fresh trial must be made, adding the bulk of the sugar at once, then finishing by drops. If, on the other hand, the sugar has been run in to excess, which owing to the rather slow reaction is easily done, fresh trial must be again made until the proper point is reached ; this gives the milk sugar. Meanwhile a measured portion of the mixed sugar solution is boiled with 2 per cent. of citric acid for at least 30 minutes.† For example, suppose that 20 c.c. of milk had been diluted to 200 c.c., 50 c.c. of the latter should be boiled with 1 gram of citric acid. The liquid is then neutralized with ammonia, made up to double its original volume, and titrated as before.

These operators have determined the reducing action of milk-, cane-, and grape-sugar on the Pavy-Fehling liquid, the result being that 100 lactose represents respectively 52 glucose or 49·4 sucrose.

F. W. Richardson and A. Jaffè‡ state that the copper method of determining mixtures of sugars in milk are practically valueless, having obtained far more consistent results by polarimetric methods.

* *Analyst* **10**, 62.

† The authors specified 10 minutes, but Watts and Tempany (*Analyst*, 1905, **30**, 119) have shown that 30-40 minutes' boiling is required.

‡ *J. S. C. I.* **23**, 309.

SULPHUR.

$S = 32{\cdot}07$.

Determination in Pyrites, Ores, Residues, etc.

1. Alkalimetric Method (Pelouze).

THIS process, designed for the rapid determination of sulphur in iron and copper pyrites, has hitherto been thought tolerably accurate, but experience has shown that it cannot be relied upon except for rough technical purposes.

The process is based on the fact that when a sulphide is ignited with potassium chlorate and sodium carbonate the sulphur is converted entirely into sulphuric acid, which expels its equivalent proportion of carbonic acid from the soda, forming neutral sodium sulphate; if therefore an accurately weighed quantity of the substance be fused with a known weight of pure sodium carbonate in excess, and the resulting mass titrated with normal acid in order to find the quantity of unaltered carbonate, the proportion of sulphur is readily calculated from the difference between the volume of normal acid required to saturate the original carbonate and that actually required after the ignition.

It is advisable to take 1 gm. of the finely levigated pyrites and 5·3 gm. of pure sodium carbonate for each assay; and as 5·3 gm. of sodium carbonate represent 100 c.c. of normal sulphuric acid, it is only necessary to subtract the number of c.c. used after the ignition from 100, and multiply the remainder by 0·016, in order to arrive at the weight of sulphur in the 1 gm. of pyrites, and by moving the decimal point two places to the right the percentage is obtained.

EXAMPLE: 1 gm. of finely ground FeS_2 was mixed *intimately* with 5·3 gm. sodium carbonate, and about 7 gm. each of potassium chlorate and decrepitated sodium chloride in powder; then introduced into a platinum crucible, and gradually exposed to a dull red heat for ten minutes; the crucible allowed to cool, and warm water added; the solution so obtained was brought on a moistened filter, the residue emptied into a beaker and boiled with a large quantity of water, brought on the filter, and washed with boiling water till all soluble matter was removed; the filtrate coloured with methyl orange, and titrated. 67 c.c. of normal acid were required, which deducted from 100, left 33 c.c.; this multiplied by 0·016 gave 0·528 gm. or 52·8 per cent. S.

Burnt Pyrites.—The only satisfactory volumetric method of determining the sulphur in the residual ores of pyrites is that described by Watson,* which is in daily use in large alkali works. In order to avoid calculation, Watson adopts the following method:—

Standard hydrochloric acid.—1 c.c. = 0·02 gm. Na_2O.

Sodium bicarbonate.—This may be the ordinary commercial salt, but its exact alkalinity must be ascertained by the standard

* *J. S. C. I.* 7, 305.

acid. Where a number of analyses are being made, a good quantity of the salt should be well mixed, and kept in a stoppered bottle. Its exact alkalinity having been once determined it will not alter, though daily opened.

METHOD OF PROCEDURE: 2 gm. of bicarbonate is placed in a crucible which may be either of platinum, porcelain, or nickel, and to it is added 5·16 gm. of the finely powdered ore, then intimately mixed with a flattened glass rod. Heat gently over a Bunsen burner for 5 or 10 minutes, and break up the mass with a stout copper wire. After stirring, the heat is increased and continued for 10 or 15 minutes. The crucible is then washed out with hot water into a beaker. The mixture is boiled for 15 minutes. filtered into a flask, the residue washed repeatedly with hot water, then cooled and titrated with the standard acid, using methyl orange as indicator.

EXAMPLE: 2 gm. of the bicarbonate originally required 37·5 c.c. of acid. After ignition with the ore, 28 c.c. were required. The difference =9·5 c.c., divided by 5 will give 1·9, which is the percentage of total sulphur in the ore.

This total sulphur includes that which exists as soluble sulphide, and which is not available for acid making. In order to find the amount of this soluble sulphur, Watson boils 5·16 gm. of the ore with 5 c.c. of standard sodium carbonate (1 c.c. = 0·05 gm. Na_2O) diluted with water, for 15 minutes. After filtering and washing, the filtrate is titrated with the standard hydrochloric acid, and the difference between the volume used and that which was originally required for 5 c.c. of the soda solution is divided by 5, as in the case of the former process, which gives at once the percentage of sulphur existing in the ore in a soluble form. The results are not absolutely exact, but quite near enough to guide a manufacturer in the working of the furnaces.

This method is not available for unburnt pyrites.

2. Determination of Sulphur in Coal Gas.

A most convenient and accurate process for this determination is that of Wildenstein (see p. 350). The liquid produced by burning the measured gas in a Letheby or Vernon Harcourt apparatus is well mixed, and brought to a definite volume; a portion representing a known number of cubic feet of gas is then poured into a glass, porcelain, or platinum basin, acidified slightly with HCl, heated to boiling, and a measured excess of standard barium chloride added; the excess of acid is then cautiously neutralized with ammonia (free from carbonate), and the excess of barium ascertained by standard potassium chromate exactly as described on p. 350.

The usual method of stating results is in grains of sulphur per 100 cubic feet of gas. This may be done very readily by using semi-normal solutions of barium chloride and potassium chromate on the metric system, and multiplying the number of c.c. of barium solution required by the factor 0·1234, which at once gives the amount of sulphur in grains.

3. Determination of Sulphur in Sulphides decomposable by Hydrochloric or Sulphuric Acid (Weil).

This process, communicated to me by M. Weil, is based on the fact that, in the case of sulphides where the whole of the sulphur is given off as H_2S by heating with HCl or H_2SO_4, the H_2S may be evolved into an excess of a standard alkaline copper solution. After the action is complete, the amount of Cu left unreduced is determined by standard stannous chloride. The method is available for the sulphides of lead, antimony, zinc, iron, etc. Operators should consult and practise the methods described on p. 198, in order to become accustomed to the special reaction involved.

METHOD OF PROCEDURE: From 1 to 10 gm. of material (according to its richness in sulphur) in the finest state of division, are put into a long-necked flask of about 200 c.c. capacity, to which is fitted a bent delivery tube, so arranged as to dip to the bottom of a tall cylinder, containing 50 or 100 c.c. of standard copper solution made by dissolving 39·523 gm. of cupric sulphate, 200 gm. of Rochelle salt, and 125 gm. of pure caustic soda in water, and diluting to 1 litre (10 c.c. = 0·1 gm. Cu). When this is ready, a few pieces of granulated zinc are added to the sulphide. 75 c.c. of strong HCl are then poured over them, the cork with delivery tube immediately inserted, connected with the copper solution, and the flask heated on a sand-bath until all evolution of H_2S is ended. The blue solution and black precipitate are then brought on a filter, filtrate and washings collected in a 200 or 250 c.c. flask, and diluted to the mark; 20 c.c. of the clear blue liquid are then measured into a boiling flask, and evaporated to 10 or 15 c.c. 25 to 50 c.c. of strong HCl are then added, and the standard tin solution dropped in while boiling, until the blue gives place to a clear pure yellow.

Each c.c. of standard copper solution represents 0·5045 gm. of sulphur. The addition of the granulated zinc facilitates the liberation of the H_2S, and sweeps it out of the flask; moreover, in the case of dealing with lead sulphide, which forms insoluble lead chloride, it materially assists the decomposition. Alkaline tartrate solution of copper may be used in place of ammoniacal solution if so desired.

EXAMPLES (Weil): 1 gm. of galena was taken, and the gas delivered into 50 c.c. of standard copper solution (= 0·5 gm. Cu). After complete precipitation the blue liquid was diluted to 200 c.c. 20 c.c. of this required 12·5 c.c. of stannous chloride, the titre of which was 16·5 c.c. for 0·04 gm. Cu. Therefore 16·5 : 0·04 : : 12·5 : 0·0303. Thus 200 c.c. (= 1 gm. galena) represent 0·303 gm. Cu. Then 0·5 gm. Cu, less 0·303 = 0·197 gm. for 1 gm. galena or 19·7 for 100 gm. Consequently $19{\cdot}7 \times 0{\cdot}5045 = 9{\cdot}94$ per cent. S. Determination by weight gave 9·85 per cent. Again, 1 gm. zinc sulphide was taken with 100 c.c. copper solution and made up to 250 c.c., 25 c.c. of which required 14·3 c.c. of same stannous chloride, or 143 c.c. for the 1 gm. sulphide. This represents 0·347 gm. Cu. Thus 1—0·347 = 0·653 gm. Cu (precipitated as CuS) or 65·3 per 100. Consequently, $65{\cdot}3 \times 0{\cdot}5045 = 32{\cdot}9$ per cent. S. Control determination by weight gave 33 per cent.

The process has given me good technical results with Sb_2S_3, but the proportion of sulphur to copper is too great to expect strict accuracy.

4. Determination of Alkali Sulphides by Standard Zinc Solution.

This method, which is simply the converse of that described under Zinc, is especially applicable for the technical determination of alkaline sulphides in impure alkalies, mother-liquors, etc.

If the zinc solution be made by dissolving 3·268 gm. of pure metallic zinc in hydrochloric acid, supersaturating with ammonia, and diluting to 1 litre, 1 c.c. will respectively indicate—

0·0016	gm.	Sulphur
0·0039	,,	Sodium sulphide
0·00551	,,	Potassium sulphide
0·0034	,,	Ammonium sulphide.

The zinc solution is added from a burette until no dark colour is shown when a drop is brought in contact with solution of nickel sulphate spread in drops on a white porcelain tile.

5. Sulphurous Acid and Sulphites.

The difficulties formerly presented in the iodimetric analyses of these substances are now fortunately quite overcome by the modification devised by Giles and Shearer.* A valuable series of experiments on the determination of SO_2, either free or combined, is detailed in these papers. The modification is both simple and exact, and consists in adding the weighed SO_2 or the sulphite in powder to a measured excess of $^N/_{10}$ iodine without dilution with water, and when the decomposition is complete, titrating back with $^N/_{10}$ thiosulphate. Very concentrated solutions of SO_2 are cooled by a freezing mixture, and enclosed in thin bulbs, which can be broken under the iodine solution: this is, however, not required with the ordinary preparations. Sulphites and bisulphites of the alkalies and alkaline earths, also of zinc and aluminium, may all be titrated in this way with accuracy; the less soluble salts, of course, requiring more time and agitation to ensure their decomposition. A preliminary titration is first made with a considerable excess of iodine, and a second with a more moderate excess as indicated by the first trial. 1 c.c. $^N/_{10}$ iodine = 0·0032 gm. SO_2.

The authors found that when perfectly pure iodine and neutral potassium iodide were used for the standard solution, its strength remained intact for a long period; and the same with the thiosulphate, if the addition of about 2 gm. of potassium bicarbonate to the litre was made, and the stock solution kept in the dark.

From a large number of experiments they also deduced the simple law of the ratio between any given percentage of SO_2 in aqueous solution at 15·4° and 760 mm., and the specific gravity; namely, the percentage found by titration multiplied by 0·005 and added to unity gives the sp. gr.

* *J. S. C. I.* **3**, 197 *and* **4**, 303.

In cases where the iodine method may not be suitable, W. B. Giles recommends the use of a standard ammoniacal silver nitrate. This process is applicable alike to SO_2, sulphites and bisulphites. The silver solution may conveniently be of $^N/_{10}$ strength, but before use ammonia is added in sufficient quantity, first to produce a precipitate of silver oxide, then to dissolve it to a clear solution. A known excess of this solution is digested in a closed bottle, with the substance, in a water-bath for some hours, the result of which is the reduction of the silver as a bright mirror on the sides of the vessel. The filtered liquid and washings may then be titrated by thiocyanate for the excess of silver, or the mirror together with any collected on the filter after washing and burning to ash may be dissolved in nitric acid and determined by the same process (p. 145). 1 c.c. $^N/_{10}$ silver = 0·0032 gm. of SO_2.

EXAMPLE: 0·1974 gm. of chemically pure potassium metabisulphite was weighed out and treated as above described, the mirror of silver and a little on the filter determined gave 0·1918 gm. of metallic silver, which multiplied by the factor 1·028 gives 0·19717 of metabisulphite or 99·9 %.

This method is very useful in determining the percentage of the SO_2 in liquefied sulphurous acid, which is now found in large quantities in commerce. By cooling down this substance to a point where it has no tension, small bulbs can be filled with facility and sealed up. After weighing they are introduced into a well-stoppered bottle containing an excess of the ammoniacal silver, and the stopper firmly secured by a clamp. By shaking the bottle vigorously the bulb is broken, and the determination is then conducted as above described.

$$Ag_2ON_2O_5 + SO_2 + xNH_3 = Ag_2 + SO_3 + N_2O_5 + xNH_3.$$

6. Analysis of Mixtures of Alkali Sulphides, Sulphites, Thiosulphates, and Sulphates.

The determination of the above-mentioned substances when existing together in any given solution presents great difficulty. Richardson and Aykroyd* have, however, published a method which seems to give fairly accurate results.

The determination of the SO_3 in such a mixture cannot be done volumetrically, but by the addition of about 5 gm. of tartaric acid to such a quantity of solution of mixed thiosulphate, sulphate, and sulphite as would be usually taken for analysis, the SO_3 may be precipitated with barium chloride in the cold. The precipitate of $BaSO_4$ contains some barium sulphite, but this is easily removed by hot dilute HCl and boiling water. The thiosulphate produces no SO_3 whatever under these circumstances, whereas in the presence of a mineral acid, sulphate is always produced.

The sulphides are determined by standard ammoniacal zinc solution, which may conveniently be of such strength that 1 c.c. = 0·0016 of S, using nickel sulphate solution as an external indicator.

* *J. S. C. I.* **15**, 171

This zinc solution is easily made from pure metallic zinc dissolved in HCl, and the precipitate which is formed by adding ammonia is brought into clear solution by a moderate excess of the same re-agent.

The zinc solution is also used for removing sulphides from a mixtures of these with thiosulphates, sulphites, and sulphates prior to the determination of the latter bodies. In this case it is only necessary to add a slight excess of the zinc solution, and filter off the precipitated sulphide.

The authors of this method after pointing out the value of Giles and Shearer's method of determining sulphites by iodine just described, mention a method devised by themselves, which enables them to determine not only sulphites but free SO_2, not only in a pure state but in mixtures with sulphates, thiosulphates, and sulphides. They avail themselves of the well-known reaction that when iodine is added to a neutral sulphite, neutral sulphate and an equivalent amount of hydriodic acid are formed.

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI,$$

and the acidity of the solution may be accurately measured by standard alkali and methyl orange.

The authors state that the best plan is to convert all sulphites to bisulphites, *i.e.*, to the hydrogen sulphite of the base : this is necessary because a sulphite may be alkaline or it may be exclusively acid. Sodium bisulphite is quite neutral to methyl orange, and by titrating the solution of a neutral sulphite with $^N/_{10}$ sulphuric acid, using methyl orange, a point is reached when all the sulphite is converted into the acid sulphite. The reason for this is patent when the reaction which takes place when an acid sulphite acts upon iodine is considered—

$$NaH.SO_3 + OH_2 + I_2 = NaH.SO_4 + 2HI.$$

Here is a new factor, inasmuch as the titration with alkali and with methyl orange as indicator is concerned ; although the acid sodium sulphite is neutral to methyl orange, the acid sodium sulphate is acid to the full and exact extent of its combining power.

Thus one molecule of sodium bisulphite, on titration with $^N/_{10}$ iodine, liberates acid equivalent to three molecules of sodium or potassium hydrate.

Example : A solution containing 1·62 per cent. of $Na_2SO_3.7Aq$ was titrated. Iodine solution equivalent to 9·5 c.c. $^N/_{10}$ I ; 29·9 c.c. were required ; the mixture required 14·6 c.c. of $^N/_{10}$ NaHO. Now 9·5 c.c. $^N/_{10}$ I and 14·6 c.c. $^N/_{10}$ NaHO are in the ratio of 2 ; 3 almost exactly ; by using 0·0126 as the factor for the c.c. of $^N/_{10}$ I and 0·084 for the $^N/_{10}$ NaHO, both results give 1·64 per cent. of $Na_2SO_3.7Aq$. (Of course the sulphite solution had been previously titrated with $^N/_{10}$ H_2SO_4 in the presence of methyl orange.)

As the details of calculation may be somewhat obscure to those who have not experimented in this direction, the working out of an actual analysis is of interest. A solution containing one per cent. of pure sodium thiosulphate, and 0·78 per cent. of sodium sulphite, was titrated upon 20 c.c. of iodine ; 19·3 c.c. were required to decolorize ; to neutralize with methyl orange as indicator 17·9 c.c. of $^N/_{10}$ soda were required ; therefore 100 c.c. of the mixture required 103·6 c.c. iodine

and 92·7 c.c. of $^N/_{10}$ soda respectively; the c.c. of soda $\times$ 0·0084 give 0·7787 as the percentage of $Na_2SO_3.7Aq$, and this figure $\div$ 0·0126 (the factor for 1 c.c. iodine in $Na_2SO_3.7Aq$) gives 61·8 c.c., and this subtracted from 103·6 c.c. of total iodine required gives 41·8 c.c., and this $\times$ 0·0248 gives 1·036 instead of 1 per cent. of $Na_2S_2O_3.5Aq$.

The advantage of this method is better seen in the case of a complex mixture, where one must remove sulphides or other bodies by the addition of an alkaline solution of zinc or other precipitating agent. The alkaline filtrate is speedily brought into a condition suitable for iodimetric and alkalimetric titration by the method proposed.

EXAMPLE: A solution of known amounts of sodium thiosulphate and sulphite was treated with 10 c.c. of a strongly ammoniacal zinc-chloride solution, and the mixture was titrated with it until it gave a neutral reaction with methyl orange; it was now made to 1000 c.c., and was titrated upon a known volume of $^N/_{10}$ iodine, using starch to find the end-reaction (which is otherwise somewhat obscured by the methyl orange). The disappearance of the blue colour and the appearance of the pinkish-purple of the acidified methyl orange is both interesting and striking. Titration with $^N/_{10}$ NaHO was now easily accomplished. The results were exact in the case of thiosulphate, and very slightly in excess in the case of sulphite.

After the sulphite and thiosulphate solution has been titrated upon a known volume of $^N/_{10}$ iodine, the sulphate formed is determined by barium at a boiling heat in the presence of a little dilute HCl. Any sulphate in the original solution is, of course, determined by the tartaric acid method and deducted from the result. Ammonium tartrate must be avoided in the process, owing to its solvent action on barium sulphate.

The process is only strictly applicable in the absence of organic matter. When that is present it is preferable to use the iodine process as follows:—

(1) *Total Iodine value of solution* $= H_2S + H_2SO_3 + H_2S_2O_3$ determined by running known volume of solution into excess of $^N/_{10}$ iodine acidified with hydrochloric acid and bringing back with $^N/_{10}$ thiosulphate. This gives $A = H_2S + H_2SO_3 + H_2S_2O_3$ accurately without loss.

(2) *Iodine value of* H S.—Add excess of ammoniacal zinc chloride, filter, wash; wash ZnS into $^N/_{10}$ iodine and hydrochloric acid (as described on page 81). This gives $B = H_2S$ accurately. Then $A - B$ gives $H_2SO_3 + H_2S_2O_3$ accurately.

(3) *Iodine value of* $H_2S_2O_3$.—To filtrate from B add acid to exactly neutralize with methyl orange as indicator.

Then titrate with iodine and starch $\quad C = H_2S_2O_3 + H_2SO_3$ *in filtrate*

Then with $^N/_{10}$ alkali ,, $\quad \frac{2}{3}$ alkali $^N/_{10}$ $D = H_2SO_3$,,

The $\frac{2}{3}$ $^N/_{10}$ alkali used = iodine equivalent of H_2SO_3 *in the filtrate* (not in the original solution, as oxidation occurs in filtration) accurately.

And $C - D = H_2S_2O_3$ accurately.

(4) *Iodine value of* H_2SO_3.—Got by difference

$$
\begin{array}{lll}
H_2SO_3 + H_2S_2O_3 = A - B & & \text{accurately} \\
H_2S_2O_3 = C - D & & ,, \\
H_2SO_3 = A - B - (C - D) & & ,,
\end{array}
$$

The procedure, so modified, is to obtain the sulphurous acid by difference in place of direct determinations. Thiosulphate suffers no appreciable oxidation on filtration; sulphite does. Hence by

determining thiosulphate and sulphide accurately sulphite is got by difference accurately. This difference figure is always rather higher than the one deduced acidimetrically (D, above.)

Another series of processes for ascertaining the proportions of mixtures of sulphuretted hydrogen, sulphurous and thiosulphuric acids has been worked out by W. Feld*. The methods described are applicable to the alkali or alkaline earth salts of the above acids, even when present in small quantities.

(1) SULPHIDES.—Alkali or alkaline earth sulphides evolve the whole of their sulphur as H_2S when boiled with a concentrated solution of magnesium chloride in an atmosphere of CO_2. The powdered and moistened sample is placed in a 300 c.c. Erlenmeyer flask provided with a doubly-bored rubber stopper. Through one hole a small tap-funnel passes to the bottom of the flask, through the other a glass tube leads to four sets of potash-bulbs in series. The last of these is connected to a 10 litre bottle acting as aspirator. The neck of the tap-funnel is connected to a supply of CO_2, which must have no action on a solution of iodine. The first set of potash-bulbs is empty, the second and third contain rather more iodine solution than will suffice to absorb all the H_2S evolved, the fourth contains $^N/_{10}$ thiosulphate solution, to take up any iodine carried over by the CO_2. About 1 litre of CO_2 is first passed, in order to displace the air in the apparatus, the tap of the funnel is then closed, and about 20 c.c. of 25 per cent. magnesium chloride solution introduced. Connection is now made to the supply of CO_2, and the magnesium chloride solution run into the flask, the contents of which are slowly heated to boiling in a current of CO_2 passing at the rate of 10 litres in three-quarters of an hour. The operation is usually ended when 5 litres have passed. The contents of the potash-bulbs are finally washed out and titrated; the reactions are—

$$BaS + MgCl_2 + CO_2 + H_2O = BaCl_2 + MgCO_3 + H_2S, \text{ and } H_2S + I_2 = 2HI + S.$$

Test analyses with $BaSH.OH + 5H_2O$ gave good results.

(2) SULPHITES are determined in the same apparatus and in the same way, hydrochloric acid taking the place of magnesium chloride.

(3) THIOSULPHATES evolve some H_2S when treated with hydrochloric acid. The following method is found, however, to give accurate results:—The thiosulphate is first converted (by titration with iodine solution) into tetrathionate. The solution of the tetrathionate, diluted with 50 c.c. of water, is placed in the flask with excess of aluminium foil, and treated, in an atmosphere of CO_2, with *dilute* hydrochloric acid in the cold. The reduction to H_2S, which is collected as before, takes place quantitatively according to the equation—

$$Na_2S_4O_6 + 20HCl + 3Al_2 = 2NaCl + 3Al_2Cl_6 + 6H_2O + 4H_2S.$$

(4) THIOSULPHATE IN PRESENCE OF SULPHITE.—This determination is made by method (3). The titration with iodine oxidizes the sulphite into sulphate, which is not affected by nascent hydrogen.

(5) SULPHITE IN PRESENCE OF THIOSULPHATE.—Excess of mercuric chloride is added to the substance; the thiosulphate is thus converted into mercuric sulphide—

$$Na_2S_2O_3 + HgCl_2 + H_2O = Na_2SO_4 + HgS + 2HCl,$$

whilst the sulphite is not affected and is determined by (2).

(6) SULPHIDE, SULPHITE, AND THIOSULPHATE.—The sample is first distilled with magnesium chloride, as described in (1). This gives the sulphide. The potash-bulbs are then refilled, excess of mercuric chloride added to the cold contents of the flask, which are then distilled with hydrochloric acid as described under (2). This gives the sulphite. The thiosulphate is determined in a fresh sample by titrating with iodine, by which the sulphide is oxidized to sulphur and the sulphite to sulphate, and then reducing by nascent hydrogen as described under (3).

* *Dic. Chem. Ind.* 1898, 372.

When, in addition to the alkali or alkaline earth salts of the acids considered, the substance contains polysulphides, free sulphur, and sulphides of the heavy metals, the difficulties are much greater, and the author is working for further information. In the meantime he has obtained satisfactory results as follows :—Free sulphur is extracted by carbon disulphide, and weighed after evaporation of the solvent. The sulphur present as sulphide is then determined by method (1). In this operation the sulphur of the polysulphides is evolved partly as H_2S, the remainder separating in the free state. The latter part is extracted by carbon disulphide. If a sulphite is present, however, some thiosulphate is formed. The solution is now titrated with iodine, during which operation the sulphur present as ferrous sulphide separates in the free state and is extracted with carbon disulphide. The solution is now treated by method (3) to determine the thiosulphate. The presence of other polythionic acids introduces an error here. In solid substances sulphites may occur in presence of polysulphides ; in this case they are determined by treatment with mercuric chloride and distillation with hydrochloric acid, according to method (2).

Lunge and Smith's methods for the same purpose are described in *J. S. C. I.* ii. 463, and also in the fifth edition of this book.

SULPHURETTED HYDROGEN.

$H_2S = 34{\cdot}09.$

1 c.c. $^N/_{10}$ arsenious solution $= 0{\cdot}002557$ gm. H_2S.

1. By Arsenious Acid (Mohr).

THIS residual process is far preferable to the direct titration of sulphuretted hydrogen by iodine. The principle is based on the fact that when H_2S is brought into contact with an excess of arsenious acid in hydrochloric acid solution, arsenic sulphide is formed ; 1 eq. of arsenious acid and 3 eq. of sulphuretted hydrogen produce 1 eq. of arsenic sulphide and 3 eq. of water,

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

The excess of arsenious acid is found by $^N/_{10}$ iodine and starch, as on p. 139. In determining the strength of sulphuretted hydrogen water the following plan may be pursued.

METHOD OF PROCEDURE : A measured quantity, say 10 c.c., of $^N/_{10}$ arsenious solution is put into a 300 c.c. flask, and 20 c.c. of sulphuretted hydrogen water added, well mixed, and sufficient HCl added to produce a distinct acid reaction ; this produces a precipitate of arsenic sulphide, and the liquid itself is colourless. The whole is then diluted to 300 c.c., filtered through a dry filter into a dry vessel, 100 c.c. of the filtrate taken out and neutralized with sodium bicarbonate, then titrated with $^N/_{10}$ iodine and starch. The quantity of arsenious acid so found is deducted from the original 10 c.c., and the remainder multiplied by the requisite factor for H_2S.

The determination of H_2S contained in coal gas may by this method be made very accurately by leading the gas very slowly through the arsenious solution, or still better, through a dilute solution of caustic alkali, then adding arsenious solution, and titrating as before described. The apparatus devised by Mohr for this purpose is arranged as follows :—

The gas from a common burner is led by means of a vulcanized tube into two successive small wash-bottles containing the alkaline solution ; from the last of

these it is led into a large Woulff's bottle filled with water. The bottle has two necks, and a tap at the bottom; one of the necks contains the cork through which the tube carrying the gas is passed; the other, a cork through which a good-sized funnel with a tube reaching to the bottom of the bottle is passed. When the gas begins to bubble through the flask, the tap is opened so as to allow the water to drop rapidly; if the pressure of gas is strong, the funnel tube acts as a safety valve, and allows the water to rise up into the cup of the funnel. When a sufficient quantity of gas has passed into the bottle, say six or eight pints, the water which has issued from the tap into some convenient vessel is measured in cubic inches or litres, and gives the quantity of gas which has displaced it. In order to ensure accurate measurement, all parts of the apparatus must be tight.

The flasks are then separated, and into the second 5 c.c. of arsenious solution are placed, and acidified slightly with HCl. If any traces of a precipitate occur it is set aside for titration with the contents of the first flask, into which 10 c.c. or so of arsenious solution are put, acidified as before, both mixed together, diluted to a given measure, filtered, and a measured quantity titrated as before described.

This method does not answer for very crude gas containing large quantities of H_2S unless the absorbing surface is largely increased.

2. By Permanganate (Mohr).

If a solution of H_2S is added to a dilute solution of ferric sulphate, the ferric salt is reduced to the ferrous state, and free sulphur separates. The ferrous salt so produced may be measured accurately by permanganate without removing the separated sulphur. Ferric sulphate, free from ferrous compounds, in sulphuric acid solution, is placed in a stoppered flask, and the solution of H_2S added to it with a pipette; the mixture is allowed to stand half an hour or so, then diluted considerably, and permanganate added until the rose colour appears. $55{\cdot}85\ Fe = 17{\cdot}04\ H_2S$

or each c.c. of $^{N}/_{10}$ permanganate represents 0·001704 gm. of H_2S. The process is considerably hastened by placing the stoppered flask containing the acid ferric liquid into hot water previous to the addition of H_2S, and excluding air as much as possible.

3. By Iodine.

Sulphuretted hydrogen in mineral waters may be accurately determined by iodine in the following manner:—

METHOD OF PROCEDURE: 10 c.c. or any other necessary volume of $^{N}/_{100}$ iodine solution are measured into a 500 c.c. flask, and the water to be examined added until the colour disappears. 5 c.c. of starch indicator are then added, and $^{N}/_{100}$ iodine until the blue colour appears; the flask is then filled to the mark with pure distilled water. The respective volumes of iodine and starch solution, together with the added water, deducted from the 500 c.c., will show the volume of water actually titrated by the iodine. A correction should be made for the excess of iodine necessary to produce the blue colour.

Fresenius* examined the sulphur water of the Grindbrunnen, in Frankfurt a. M., both volumetrically and gravimetrically for H_2S with very concordant results. 361·44 gm. of water (correction for blue colour being allowed) required 20·14 c.c. of iodine, 20·52 c.c. of which contained 0·02527 gm. of free iodine $= H_2S$ 0·0092 gm.

* *Z. a. C.* 14, 321.

per million. 444·65 gm. of the same water required, under the same conditions, 25·05 c.c. of the same iodine solution = H_2S 0·0092 gm. per million. Gravimetrically the H_2S was found to be 0·0094 gm. per million.

SULPHURIC ACID AND SULPHATES.

Monohydrated Sulphuric Acid.

$H_2SO_4 = 98{\cdot}086.$

Sulphuric Anhydride.

$SO_3 = 80{\cdot}07.$

1. Mohr's Method.

In my opinion the determination of sulphuric acid in most cases is more easily obtained by gravimetric than by volumetric methods, but there are circumstances in which the latter are useful. The indirect process devised by C. Mohr* consists in adding a known volume of barium solution to the compound, more than sufficient to precipitate the SO_3. The excess of barium is converted into carbonate, and titrated with normal acid and alkali.

Normal barium chloride is made by dissolving 122·161 gm. of pure crystals of chloride in the litre; this solution likewise suffices for the determination of SO_3 by the direct method.

Method of Procedure: If the substance contains a considerable quantity of free acid, it must be brought nearly to neutrality by adding pure sodium carbonate; if alkaline, slightly acidified with hydrochloric acid; a round number of c.c. of barium solution in excess is then added, and the whole digested in a warm place for some minutes; the excess of barium is precipitated by a mixture of carbonate and caustic ammonia in slight excess; if a piece of litmus paper be thrown into the mixture, a great excess may readily be avoided. The precipitate containing both sulphate and carbonate is now to be collected on a filter, thoroughly washed with boiling water, and titrated.

The difference between the number of c.c. of barium solution added and that of normal acid required for the carbonate will be the measure of the sulphuric acid present; each c.c. of barium solution is equal 0·040 gm. SO_3.

Example: 2 gm. of pure and dry barium nitrate and 1 gm. of pure potassium sulphate were dissolved separately, mixed, and precipitated hot with carbonate and free ammonia; the precipitate, after being thoroughly washed, gave 1·002 gm. potassium sulphate, instead of 1 gm.

For technical purposes this process may be considerably shortened by the following modification, which dispenses with the washing of the precipitate.

The solution containing the sulphates or sulphuric acid is first rendered neutral; normal barium chloride is then added in excess, then normal sodium carbonate in excess of the barium chloride, and the volume of both solutions noted; the liquid is then made up to 200 or 300 c.c. in a flask, and an aliquot portion filtered off and titrated with normal acid. The difference between the barium chloride and sodium carbonate gives the sulphuric acid.

* *Ann. der Chem. u. Pharm.* **90**, 165.

The solution must of course contain no substance precipitable by sodium carbonate except barium (or if so, it must be previously removed); nor must it contain any substance precipitable by barium, such as phosphoric or oxalic acid, etc.

2. Titration by Barium Chloride and Potassium Chromate (Wildenstein).

To the hot solution containing the SO_3 to be determined (which must be neutral,—or if acid, neutralized with ammonia free from carbonate), a standard solution of barium chloride is added in slight excess, then a solution of potassium chromate of known strength is cautiously added to precipitate the excess of barium. So long as any barium remains in excess, the supernatant liquid is colourless; when it is all precipitated the liquid is yellow, from the potassium chromate; a few drops only of the chromate solution are necessary to produce a distinct colour.

Wildenstein uses a barium solution, of which 1 c.c. = 0·015 gm. SO_3, and chromate 1 c.c. = 0·010 gm. of SO_3. I prefer to use $^N/_2$ solutions, so that 1 c.c. of each is equal to 0·02 gm. of SO_3. If the chromate solution is made of equal value to the barium chloride, the operator has simply to deduct the one from the other, in order to obtain the quantity of barium solution really required to precipitate all the SO_3.

Method of Procedure: The substance or solution containing SO_3 is brought into a small flask, diluted to about 50 c.c., acidified if necessary with HCl, heated to boiling, and precipitated with a slight excess of standard barium chloride delivered from the burette. As the precipitate rapidly settles from a boiling solution, it is easy to avoid any great excess of barium, which would prevent the liquid from clearing so speedily. The mixture is then cautiously neutralized with ammonia free from carbonic acid (to be certain of this, it is well to add to it two or three drops of calcium chloride or acetate solution).

The flask is then heated to boiling, and the chromate solution added in ½ c.c. or so, each time removing the flask from the heat and allowing to settle until the liquid is of a light yellow colour; the quantity of chromate is then deducted from the barium solution, and the remainder calculated to SO_3.

Or the mixture with barium in excess may be diluted to 100 or 150 c.c., the precipitate allowed to settle thoroughly, and 25 or 50 c.c. of the clear liquid heated to boiling, after neutralizing, and precipitated with chromate until all the barium is carried down as chromate, leaving the liquid of a light yellow colour; the analysis should be checked by a second titration. The process has yielded me very satisfactory results in comparison with the barium method by weight; it is peculiarly adapted for determining sulphur in gas when burnt in the Letheby sulphur apparatus, details of which will be found on p. 340.

The presence of alkali and alkaline earthy salts is of no consequence—Zn and Cd do not interfere—Ni, Co, and Cu give coloured solutions which prevent the yellow chromate being seen, but this difficulty can be overcome by the use of an external indicator for showing the excess of chromate. This indicator is an ammoniacal lead solution, made by mixing together, at the time required, one volume of pure ammonia and four volumes of lead acetate solution (1 : 20). The liquid has an opalescent appearance. To use the indicator, a large drop is spread upon a white

porcelain plate, and one or two drops of the liquid under titration added; if the reddish-yellow colour of lead chromate is produced, there is an excess of chromate, which can be cautiously reduced by adding more barium until the exact balance is reached.

A variation of the chromate method has been devised by Andrews,* which is especially serviceable for determining the combined SO_3 in alkali salts. The method is strongly recommended by Reuter† as simple and easy of execution.

METHOD OF PROCEDURE: 3 or 4 gm. of pure precipitated barium chromate are dissolved in 30 c.c. of strong hydrochloric acid, and the whole is diluted to 1 litre. The liquid to be tested, which should contain about 0·07 gm. of SO_3 as an alkali sulphate, is mixed at the boiling point with an excess (150 c.c.) of the chromate solution; the acid is neutralized with pure powdered chalk, and the precipitate is removed by filtration. After thorough cooling, the filtrate is acidified with 5 c.c. (not more) of strong HCl, 20 c.c. of a 10 per cent. solution of potassium iodide are added, and the liquid is allowed to rest for five minutes in a covered beaker and in an atmosphere of carbonic acid (to prevent oxidation of the HI) until the chromic acid is entirely reduced. Finally, it is diluted to 1 or 1½ litre, and titrated quickly with thiosulphate; three atoms of iodine corresponding to 1 molecule of SO_3.

Another variation of the chromate method has been devised by Mitchell and Smith.‡ It consists in using excess of standard ammonium dichromate, and titrating the excess by means of standard ferrous ammonium sulphate.

METHOD OF PROCEDURE:—A convenient quantity of a sulphate is taken and dissolved in water or pure hydrochloric acid, or, if necessary, dilute nitric acid, and a slight excess of standard (2 $^N/_5$) solution of barium chloride is added. The mixture is boiled and rendered neutral by ammonium hydroxide; sodium acetate, acetic acid, and a slight excess of $^N/_{10}$ ammonium dichromate are added. The mixture is made up to 100 c.c., and the precipitate allowed to settle; 25 c.c. of the clear supernatant liquid are titrated with $^N/_{20}$ ferrous ammonium sulphate, using potassium ferricyanide as an external indicator, and taking the first appearance of a green tinge as the end-point.

It should be noted that ammonium dichromate, which is $^N/_{10}$ in respect of oxidizing power, is only $^N/_{30}$ in respect of precipitating power.

The method appears to be rapid, and the authors' results are very accurate.

3. Direct Precipitation with Normal Barium Chloride.

Very good results may be obtained by this method when carefully performed.

METHOD OF PROCEDURE: The substance in solution is to be acidified with hydrochloric acid, heated to boiling, and the barium solution allowed to flow cautiously in from the burette until no further precipitation occurs. The end of the process can only be determined by filtering a portion of the liquid, and testing with a drop of the barium solution. Beale's filter (shown in fig. 23) is a good aid in this case. A few drops of clear liquid are poured into a test tube, and a drop of barium solution added from the burette; if a cloudiness appears, the contents of the tubes must be emptied back again, washed out into the liquid, and more barium solution added until all the SO_3 is precipitated. It is advisable to use $^N/_{10}$ solution towards the end of the process.

* *Amer Chem. Jour.* 1880, 567. † *Chem. Zeit.* 1898, 357.

‡ *J. Chem. Soc.* 1909, **95**, 2198.

Instead of the test tube for finding whether barium or sulphuric acid is in excess, a plate of black glass may be used, on which a drop of the clear solution is placed and tested by either a drop of barium chloride or sodium sulphate,—these testing solutions are preferably kept in two small bottles with elongated stoppers. A still better plan is to spot the liquids on a small mirror, as suggested by Haddock;* the faintest reaction can then be seen, although the liquid may be highly coloured.

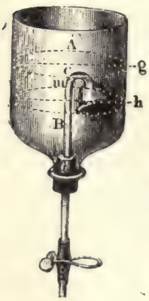


Fig. 54.

Wildenstein has arranged another method for direct precipitation, especially useful where a constant series of determinations have to be made. The apparatus is shown in fig. 54. A is a bottle of 900 or 1000 c.c. capacity, with the bottom removed, and made of well-annealed glass so as to stand heating; B a thistle funnel bent round, as in the figure, and this siphon filter is put into action by opening the pinch-cock below the cork. The mouth of the funnel is first tied over with a piece of fine cotton cloth, then two thicknesses of Swedish filter-paper, and again with a piece of cotton cloth, the whole being securely tied with waxed thread.

In precipitating SO_3 by barium chloride, there occurs a point similar to the so-called neutral point in silver assay, when in one and the same solution both barium and sulphuric acid after a minute or two produce a cloudiness. Owing to this fact, the barium solution must not be reckoned exactly by its amount of $BaCl_2$, but by its working effect; that is to say, the process must be considered ended when the addition of a drop or two of barium solution gives no cloudiness after the lapse of two minutes.

METHOD OF PROCEDURE.—The solution containing the SO_3 having been prepared, and preferably in HCl, the vessel A is filled with warm distilled water and the pinch-cock opened so as to fill the filter to the bend C; the cock is then opened and shut a few times so as to bring the water further down into the tube, but not to fill it entirely; the water is then emptied out of A, and about 400 c.c. of boiled distilled water poured in together with the SO_3 solution, then, if necessary, a small quantity of HCl added, and the barium chloride added in moderate quantity from a burette. After mixing well, and waiting a few minutes a portion is drawn off into a small beaker, and poured back without loss into A; a small quantity is then drawn off into a test tube, and two drops of barium chloride added. So long as a precipitate is produced the liquid is returned to A, and more barium added until a test is taken which shows no distinct cloudiness; the few drops added to produce this effect are deducted. If a distinct excess has been used, the analysis must be corrected with a solution of SO_3 corresponding in strength to the barium solution.

A simpler and even more serviceable arrangement of apparatus on the above plan may be made by using as the boiling and precipitating vessel an ordinary beaker standing on wire gauze or a hot plate. The filter is made by taking a small thistle funnel, tied over as described, with about two inches of its tube, over which is tightly slipped about four or five inches of elastic tubing,

* C. N 32, 156

terminating with a short piece of glass tube drawn out to a small orifice like a pipette ; a small pinch-cock is placed across the elastic tube just above the pipette end, so that when hung over the edge of the beaker with the funnel below the surface of the liquid, the apparatus will act as a siphon. It may readily be filled with warm distilled water by gentle suction, then transferred to the liquid under titration, By its means much smaller and more concentrated liquids may be used for the analysis, and consequently a more distinct evidence of the reaction obtained.

4. Determination by Benzidine Hydrochloride.*

Benzidine sulphate $C_{12}H_8(NH_2)_2 . H_2SO_4$ is a stable salt almost insoluble in water containing hydrochloric acid. Benzidine being a weak organic base, neutral to phenolphthalein, the acid in its sulphate can be titrated with standard alkali. For the determination of sulphuric acid by benzidine Raschig† recommends treating the neutral or acid solution of the sulphate with benzidine hydrochloride solution, filtering off the precipitated benzidine sulphate, washing it, and then suspending it in water and titrating the sulphuric acid with $^N/_{10}$ soda.

METHOD OF PROCEDURE:—To prepare the solution of benzidine hydrochloride, 6·7 gm. of the free base, or the corresponding amount of the hydrochloride, is rubbed up in a mortar with 20 c.c. of water. The paste is rinsed into a litre flask, 20 c.c. of hydrochloric acid (sp. gr. 1·12) are added, and the solution diluted to the mark. (1 c.c. of this solution corresponds theoretically to 0·00357 gm. H_2SO_4.) The solution has a brown colour and may be filtered if necessary. After some time brown flakes are likely to separate, but these do no harm.

The solution of the sulphate is diluted with water until its volume corresponds to not less than 50 c.c. for each 0·1 gm. of sulphuric acid present. An equal volume of the reagent is added while stirring vigorously. A filter is prepared by placing a perforated porcelain filter plate in a funnel and covering it with two moistened filter papers, one of exactly the same size as the plate and the upper one a little larger. After ten minutes, the precipitate is filtered off upon this filter, using gentle suction. The last portions of the precipitate are transferred to the filter with the aid of small portions of the clear filtrate, and then the beaker and precipitate are washed with 20 c.c. of cold water, added in several portions. The precipitate and filter, but not the plate, are then transferred to an Erlenmeyer flask, 50 c.c. of water are added and the contents of the stoppered flask shaken until a homogeneous paste is obtained. The rubber stopper is then removed, rinsed with water, a drop of phenolphthalein added, the water heated to about 50° C, and titrated with $^N/_{10}$ sodium hydroxide. When the end point is nearly reached, the liquid is boiled for five minutes, and the titration then finished.

According to Friedheim and Nydegger,‡ this method gives excellent results in the analysis of all sulphates, provided no substances are present which attack benzidine, and provided the amount of other salts and acids present is not too great. There should not be more than 10 mol. of HCl, 15 mol. HNO_3, 20 mol. $HC_2H_3O_2$, 5 mol. alkali salt, or 2 mol. ferric iron present to 1 mol. H_2SO_4. A satisfactory determination of the sulphur in pyrites

*See Treadwell's *Analytical Chemistry*, translated by Hall, 2nd edition, Vol. II., p. 658.

† *Z. a. Chem.* 1903, 617 and 818. ‡ *Z. a. Chem.* 1907, 9.

may be made by dissolving 0·5 gm. of the sample according to the Lunge method, evaporating off the nitric acid, taking up the residue in a little hydrochloric acid, diluting to 500 c.c. and using 100 c.c. for the treatment with benzidine hydrochloride.

PERSULPHATES.

The alkali persulphates may be readily titrated by adding to their solution a known excess of ferrous salt and determining the amount of oxygen absorbed by titration of the solution with permanganate. The salt, say potassium persulphate, decomposes as follows :—

$$K_2S_2O_8 = K_2SO_4 + SO_2 + O_2.$$

The operation requires a standard permanganate, whose value is known upon a solution of ammonio-ferrous sulphate, containing about 30 gm. per litre. The method adopted by Le Blanc and Eckardt* is to dissolve about 2·5 gm. of the persulphate in water and dilute to 100 c.c. 10 c.c. of this solution are placed in a flask with 5 c.c. of dilute sulphuric acid of 1·16 sp. gr., and a considerable excess of ferrous solution, say 100 c.c., then about 100 c.c. of distilled water at a temperature of 70° to 80° C. are added, and a rapid titration made with permanganate. The reaction is the more rapid the greater the excess of iron solution, within reasonable limits.

The standard solutions are best verified upon a persulphate of known purity in order to ascertain the comparative composition of any given sample.

Another method consists in decomposing the persulphate by means of potassium iodide, and titrating the iodine separated with thiosulphate solution. 2 to 3 gm. of the sample are dissolved in 100 c.c. of water, and 10 c.c. of the solution are treated with an excess of potassium iodide (0·25 to 0·50 gm.), and heated for 10 minutes in a drying oven at 60° to 80° C. The iodine is then titrated with $^{N}/_{10}$ thiosulphate, starch being added towards the end of the titration. In this case the effects of the process are best established upon a persulphate of known purity.

B. Grützner† has discovered that arsenious acid is completely oxidized to arsenic acid by alkali persulphates in alkaline solution.

In applying this reaction, about 0·3 gm. of the alkali persulphate is heated gradually to boiling with 50 c.c. of $^{N}/_{10}$ As_2O_3 and a few c.c. of potash or soda-lye, then digested for a short time, allowed to cool, the liquid made faintly acid with sulphuric acid, then strongly alkaline with sodium bicarbonate, and the excess of arsenious acid titrated back with $^{N}/_{10}$ iodine solution.

Marie and Bunel‡ from careful experiments advocate the following method for alkali persulphates :—

* *C. N.* **81**, 38. † *Chem. Centr.* 1900, 435. ‡ *Bull. Soc. Chim.* **29**, *No.* 18.

Dissolve about 0·3 to 0·4 gm. of the sample in 100 c.c. of water; neutralize the solution, which is generally acid, in the presence of methyl orange; then add 2 c.c. of methylic alcohol, heat for five minutes to 70—80°, and then boil for ten minutes, cool, and titrate with methyl orange and decinormal soda.

1 c.c. of decinormal soda corresponds to 0·0135 gm. $K_2S_2O_8$.
1 ,, ,, ,, ,, 0·0119 ,, $Na_2S_2O_8$.
1 ,, ,, ,, ,, 0·0114 ,, $Am_2S_2O_8$.

The use of methyl alcohol is based on the fact that a persulphate transforms a portion of the alcohol into aldehyde according to a well-known reaction. The method gave very satisfactory results.

TANNIC ACID.

THE determination of tannin in the materials used for tanning is by no means of the most satisfactory character. Many methods have been proposed, and given up as practically useless. Löwenthal's method, with later variations, is accepted as the best volumetric method; but it is still deficient in accuracy and reliability, although much ingenuity and intelligence have been expended on it.

One difficulty is still unsurmounted, and that is the preparation of a pure tannic acid to serve as standard. The various tannins in existence are still very imperfectly understood,* but so far as the comparative analysis of tanning materials among themselves is concerned, the method in question is theoretically the best.

The principle of the method depends on the oxidation of the tannic acid, together with glucosides and other easily oxidizable substances, by permanganate, regulated by the presence of soluble indigo, prepared from what is commonly called indigo carmine, but is chemically sulphindigotate of sodium or potassium, which also acts as an indicator of the end of the reaction. The total amount of such substances having been found and expressed by a known volume of permanganate, the actually available tannin is then removed by gelatine, or by the hide-powder system, and the second titration is made upon the solution so obtained in order to find the amount of oxidizable matters other than tannin.

The volume of permanganate so used, deducted from the volume used originally, shows the amount of tannin actually available for tanning purposes expressed in terms of permanganate.

H. R. Procter in his *Leather Industries Laboratory Book* gives the most recent methods of using this process in the Yorkshire College where he is the professor of leather manufacture, and

* Von Schröder, whose suggestions have been adopted by the German Association of Tanners, selects a commercial pure tannic acid for use as a standard by dissolving 2 gm. in a litre of water. 10 c.c. of this is titrated with permanganate as described. 50 c.c. are then digested twenty hours with 3 gm. moistened hide-powder. 10 c.c. of the filtrate from this is then titrated, and if the permanganate consumed amounts to less than 10 per cent. of the total consumed by the tannin, it is suitable for a standard. 1000 parts being considered equivalent in reducing power to 1048 parts of tannin precipitable by hide, according to Hammer's experiments, therefore Von Schröder, after titrating as described, calculates the dry matter, and multiplies by the round number 1·05 to obtain the value in actual tannin precipitable by hide.

gives his opinion of its value as a practical process. "It is now much superseded by the hide-powder method, but there are still a few cases in which it may be employed with advantage. Where only one or two analyses are to be made at one time, the preparation and adjustment of solutions is much more tedious than gravimetric analysis, but where a number of successive titrations are required it is considerably more rapid. It has the advantage that it can be applied direct to solutions however dilute, and if gelatine precipitation is used, it is much less affected by the presence of gallic acid or other fixed acids than the hide-powder method, and is therefore well adapted for the analysis of weak and waste liquors for technical purposes, for the systematic testing of spent tans, and for the analysis of sumach and myrabolans which contain much gallic acid, and which in the gravimetric method is wholly or partially estimated as tanning matter."

The extraction of the tannic acid from the raw material is best performed by making an infusion of the ground substance first with distilled water to about 500 c.c. at a temperature not greater than 50° C. then with water at 100° C., and percolating till free from tannin, and diluting when cold to 1 litre. Portions are filtered if necessary. Concentrated extracts are dissolved before titration by adding them to boiling water, then cooling and diluting to the measure. In the case of strong materials such as sumach or valonia 10 gm., or oak bark 20 gm., are used.

The quantity of these extracts to be used for titration must be regulated to some extent by the amount of permanganate required to oxidize the tannic and gallic acids present. Practice and experience will enable the operator to judge of the proper proportions to use in dealing with the various materials, bearing in mind that volumetric processes are largely dependent upon identity of conditions for securing concordant results. The recommendation of the best authorities is that the strength of the solution used for titration should be such as to give a solid residue of from 0·6 to 0·8 gm. from 100 c.c.

The working details according to Procter adopted at the Yorkshire College are as follows. The solutions required are :—

(1) Pure potassium permanganate, 0·5 gm. per litre. As very weak solutions do not keep well, it is best to make up one of 5 gm. per litre, and dilute when wanted. The exact strength of the permanganate is not important so long as it is constant through a series of experiments.

(2) Pure indigo-carmine 5 gm., and concentrated H_2SO_4, 50 gm. per litre. This must be filtered, and should give a pure yellow free from any trace of brown where oxidized with permanganate ; 25 c.c. of this solution should equal about 30 c.c. of the permanganate, and, if necessary, must be diluted to that strength.

(3) Solution of pure tannin, 3 gm. to 1 litre. Since absolutely pure tannin cannot be obtained, the following method is adopted :— A sample of the purest obtainable tannin (not less than 90-95 per

cent. pure by hide-powder) is preserved air-dry in a well-stoppered bottle, and the moisture carefully determined. The principal impurity is gallic acid, which acts on permanganate like tannin, but reduces somewhat more strongly, and 1 part of such tannin, calculated to dry weight, is equal on the average to 1·05 parts of pure tannin. Hence it is easy to calculate a quantity of the air-dry tannin equal in permanganate value to 0·3 gm. of pure tannin, and this is weighed out when required and made up to 100 c.c. The moisture varies very little, but it is well occasionally to re-determine it and calculate afresh.

METHOD OF PROCEDURE: 25 c.c. of the indigo solution are mixed in a beaker with about ¾ litre of clean tap water, and the permanganate added drop by drop from a glass-tapped burette till a pure yellow is obtained, the liquid being stirred steadily the whole time. A disc stirrer or a glass rod bent several times back and forward, is to be preferred to a plain rod; or some method of mechanical stirring may be adopted. The dropping should be always as nearly as possible at a similar rate for each experiment, and should be slower towards the end of the titration. It is convenient to keep a second beaker titrated to a pure primrose yellow as a standard test. Titrations may be accurately performed by artificial light, but usually differ slightly from those by daylight, and hence the light should not be varied in the course of an analysis. For daylight work Kathreiner recommends the use of a white basin instead of a beaker. The permanganate solution is allowed to drop in, with constant stirring, till the pure yellow liquid shows a faint pinkish rim, most clearly seen on the shaded side. This end-reaction is of extraordinary delicacy, and is quite different from the pink caused by excess of permanganate, being an effect common to all pure yellow liquids. The titration is done at least twice, and the average taken; ¾ litre of water and 25 c.c. of indigo are then taken as before, and 5 c.c. of the tannin solution are added and similarly titrated repeatedly. Deducting amount required for the indigo, the remainder is that consumed by the tannin, which should not at most exceed two-thirds of that required by the indigo. A similar titration is made with the tannin infusion to be examined, of which such a number of cubic centimetres is employed as will consume about the same quantity of the permanganate as the standard tannin solution. The value of the total astringent is then calculated in terms of tannin.

Since tanning matters contain astringents which are not taken up by the hide, but which are oxidized by permanganate like tannins, it is in most cases necessary to remove the tannin from a portion of the infusion, and to repeat the titration to determine the non-tannin ingredients.

This may be done by the hide-powder method at the same time that the tannin substance is determined gravimetrically, but a much quicker and even better method is that of Hunt. The solutions required are:—

(1) Pure gelatin, 2 gm. per 100 c.c.

(2) Saturated solution of NaCl containing 50 c.c. of concentrated H_2SO_4 per litre.

METHOD OF PROCEDURE: To 50 c.c. of the liquor (of about the strength of 1 to 1·5 gm. of tannin per 100 c.c.) are added 25 c.c. of the gelatin solution and 25 c.c. of the salt solution, and about a teaspoonful of kaolin or barium sulphate, and the whole is well shaken for five minutes and filtered. This filtrate, which should be perfectly bright, is titrated for non-tannin bodies by the permanganate method, double the volume being taken which was employed for determination of total astringents, and the result is deducted before calculating the tanning value.

It is impossible to give here the opinions held by various authorities on this subject, therefore the reader who desires fuller

information should consult the various papers contributed to various journals, etc., and more especially Procter's book before mentioned.

The table below by Hunt is appended, as the result of careful working, and as a guide to the nature of various tanning materials :—

The "total extract" in the table was determined by evaporating a portion of the tannin solution to dryness in a small porcelain basin and drying the residue at 110° C. The "insoluble matter" was also dried at 110° C.

The hide-powder process for tannin not being a volumetric one is not described here.

NAME OF MATERIAL.	Total matters oxidized by Permanganate, as Oxalic Ac.	Tannin, as Oxalic Ac. (Procter)	Tannin, as Oxalic Ac. (Hunt)	Total Extract.	Insoluble.
	per cent.	per cent.	per cent.	per cent.	per cent.
English Oak Bark	15·70	13·54	11·97	18·38	66·15
Canadian Hemlock Bark	9·03	7·46	7·08	13·96	75·25
Larch Bark	8·20	7·17	6·15	20·64	60·80
Mangrove Bark	31·35	29·71	28·48	26·60	49·70
Alder Bark	8·27	6·15	5·73	19·36	68·00
Blue Gum Bark	10·18	8·91	8·91	11·76	74·65
Valonia	37·41	35·24	30·50	38·50	46·05
Myrabolans	48·23	38·43	38·00	42·80	—
Sumach	42·53	34·30	31·46	44·10	47·77
Betel Nut	15·91	13·87	13·79	17·94	67·00
Turkish Blue Galls ..	73·38	65·83	59·96	48·40	36·35
Aleppo Galls	98·85	87·82	83·05	68·80	14·32
Wild Galls	26·21	18·75	16·56	31·70	54·17
Divi-Divi	66·98	62·62	61·22	54·38	29·90
Balsamocarpan (poor and old sample)	50·49	37·76	32·88	57·14	28·25
Pomegranate Rind	27·58	24·18	23·12	41·00	49·50
Tormentil Root	22·27	20·98	20·68	19·70	67·95
Rhatany Root	22·27	20·15	19·30	18·80	66·00
Pure Indian Tea	23·06	18·65	17·40	34·46	53·40
Pure China Tea	18·03	14·21	14·09	24·50	62·60
Cutch	57·65	51·95	44·24	61·60	4·75
Gum Kino	66·39	59·55	51·55	79·30	1·00
Hemlock Extract	35·16	33·17	30·98	48·78	—
Oakwood Extract	33·49	26·90	23·86	37·78	—
Chestnut Extract	39·77	32·63	28·88	50·28	—
Quebracho Extract ..	48·22	34·45	40·84	49·00	—
"Pure Tannin"	135·76	122·44	121·93	—	—
Tan Liquor, sp. gr. 1·030	4·84	3·14	2·10	6.01	—
Spent Tan Liquor, sp. gr. 1·0165	1·40	0·37	0·25	3·10	—
			Absorbed by Dry Pure Skin.		
Gambier, Cube	70·12	—	51·07	74·40	5·31
,, Sarawak	63·13	—	47·09	70·70	3·67
,, Bale	56·00	—	43·70	63·54	1·40

Tannin in Tea.—The extract of this substance is made upon 10 gm. of the tea, by boiling with a litre of distilled water for an hour in a flask fitted with a reflux condenser, filtering and diluting the liquid when cool to a litre.

A. H. Allen remarks that the determination of tannin in tea affords valuable information respecting the probable presence of previously infused leaves or extraneous tannin matters, such as catechu. This is best effected in the aqueous decoction obtained by exhausting the sample with boiling water, as required for the determination of the extract.

The tannin may be determined by the modification of Löwenthal's process, as previously described. A volume of the above decoction corresponding to 0·04 gm. of tea may be taken for the original titration with permanganate; and of the decoction deprived of tannin a volume corresponding to 0·080 gm. of tea. The tannin of tea is stated by some chemists to be gallotannic acid, and by others to be identical with that of oak bark. The reduction-equivalent of the latter is almost identical with that of crystallized oxalic acid, so that the weight of this substance corresponding to the volume of permanganate decolorized gives without calculation that of the tannin present.

The process of fermentation to which black tea has been subjected undoubtedly causes modification of the tannin, with formation of dark-coloured insoluble matter. The author found that a decoction of green tea precipitated ferric chloride bluish-black, like nut-galls, while that of black tea gave a green colour with iron, just as catechu does.

A. H. Allen in his *Organic Analysis*, vol. iii. part 2, gives a modification of the lead method.

The Löwenthal process distinguishes the tannic acid from the small quantity of gallic acid also present in tea, but as the astringent character of the infusion is due to both these substances, a method which will determine the total amount of astringent matter, without distinction of its nature, is in some respects preferable to a process that gives merely the amount of tannin, while ignoring the gallic acid. Such a process was devised by F. W. Fletcher and A. H. Allen* in 1874, and was based on the precipitation of the tea infusion by lead acetate, and the use of an ammoniacal solution of potassium ferricyanide to indicate the complete precipitation of the astringent matters.

Method of Procedure: 5 gm. of neutral acetate of lead should be dissolved in distilled water, and diluted to 1 litre, and the solution filtered after standing. The indicator is made by dissolving 0·050 gm. of pure potassium ferricyanide in 50 c.c. of water, and adding an equal bulk of strong ammonia solution. This reagent gives a deep red coloration with gallotanic acid, gallic acid, or an infusion of tea. One drop of the solution will detect 0·001 milligram of tannin. In carrying out the process, three separate quantities of 10 c.c. each of the standard lead solution should be placed in beakers, and each quantity diluted to about 100 c.c. with boiling water. A decoction made from 2 gm. of powdered tea in

* *C. N.* **29**, 169, 189.

250 c.c. of water (the same as is used for determining the extract) is added from a burette, the first trial quantity receiving an addition of 10, the second 15, and the third 18 c.c.; or if green tea be under examination, 8, 10, and 12 c.c. may be preferably employed. 1 c.c. each of these trial quantities are passed through small filters, and the filtrates tested with ammoniacal ferricyanide solution.

The approximate volume of tea decoction required is thus easily found, and after repeating the test nearly the requisite measure can be at once added. In this case about 1 c.c. of the liquid should be removed with a pipette, passed through a small filter, and drops of the filtrate allowed to fall on to spots of the indicating solution previously placed on a porcelain slab. If no pink coloration is observed, another small addition of the tea decoction is made, a few drops of the liquid filtered and tested as before, and this process repeated until a pink colour is observed. The greatest delicacy is obtained when the drops of filtered solution are allowed to fall directly on to the spots of the indicator, instead of observing the point of junction of the liquids.

The volume of tea solution it is necessary to add to 100 c.c. of pure water, in order that a drop may give a pink reaction with the indicator, should be subtracted from the total amount run from the burette.

The foregoing process is simple, and gives very concordant results; but the repeated filtrations requisite for the observation of the end-reaction are apt to be tedious. It is difficult to obtain pure tannin for setting the lead solution, and hence it is preferable to abandon the attempt and make pure lead acetate the starting-point. The author found that 10 c.c. of the lead solution would precipitate 0·010 gm. of the purest gallotannic acid he could obtain. Hence, if all the weights and measures above mentioned be adhered to, the number of c.c. of tea decoction required, divided into 125, will give the percentage of tannin and other precipitable matters in the sample. The proportion found in undried black tea by F. W. Fletcher and the author ranged from 8·5 to 11·6 per cent., with an average of 10 per cent.

Tannin in Wine, Cider, etc.—The method now generally adopted for this determination is that of treating a known volume of the wine, etc., with catgut (violin strings which have not been oiled, and which have been purified by washing in dilute alcohol, acid, and water until they have no reducing action on permanganate in the cold). The digestion is carried on at ordinary temperature for a week, in a closely stoppered bottle. The original substance, and that from which the tannin has been removed, are then titrated with permanganate, and the difference calculated to tannin.

Another method consists in mixing equal parts of an eighth per cent. solution of alum and the wine, collecting the precipitate on a filter, washing slightly with cold water, transferring the precipitate by a stream of water from a wash-bottle to a beaker, then acidifying with H_2SO_4 and titrating with indigo and permanganate as usual.

Dreaper's Copper Process for Tannic and Gallic Acids.—This is described in a paper contributed to *J. C. S. I.* xii. 412, from which the following abstract is taken.

The methods hitherto proposed for the determination of tannin may be divided into two classes, viz.:—

(1) Those which act by precipitating the tannic acid as an insoluble compound.

(2) Those which act by oxidation.

To the former class belongs the well-known hide-powder process, and to the latter Löwenthal's permanganate method, which has been modified by Procter and others. These fairly represent the two classes, and are the only ones in general use at the present day.

Dreaper, however, has adopted a modified form of Darton's method, the novelty of which consists in precipitating the tannic acid by means of an ammonio-copper sulphate solution, after a preliminary treatment with sulphuric acid to remove the ellagic acid, and then a treatment with ammonia, filtering after each treatment. Procter states that this preliminary treatment is unnecessary in the case of some extracts, but Dreaper has never found any precipitation to take place in the case of the so-called pure tannic acids, probably owing to the removal of the impurities during the process of purification. The original solution and the filtrate are titrated with permanganate as in Löwenthal's method, the difference in the two results being due to the tannic acid present. The copper compound may be dried at 110° C. and weighed, or else ignited and weighed as copper oxide. Fleck states that the tannic acid can be calculated from this by multiplying by the factor 1·034.

The standard copper solution used by the author contained 30 gm. of pure crystallized copper sulphate in a litre of water. Barium carbonate is also required, which should be free from calcium salts.

The process is based on the direct precipitation of the gallic and tannic acids by means of a copper salt, using as outside indicator potassium ferrocyanide. If a standard solution of copper sulphate be run into a solution of the mixed acids, a certain amount of copper tannate and gallate will be precipitated, depending on the dilution of the solution and the amount of acid set free from the copper sulphate. The precipitate is, under these circumstances, of a bulky nature and ill adapted to any separation by quick filtration, so necessary in a process of this description. It was found that when a solution of copper sulphate was added to a solution of the mixed acids in the presence of barium carbonate, the precipitation proceeds with the utmost regularity. The carbonate immediately forms insoluble sulphate with the free acid, and also helps to consolidate the precipitated copper salts, so that towards the end of the reaction they fall rapidly to the bottom of the vessel, leaving the supernatant liquid clear. This separation is a good indication that the end of the titration is near, and is supplemented by the ferrocyanide test.

A molified method of testing for the excess of copper in the solution is as follows:—Pieces of stout Swedish filter-paper one inch square are folded across the middle, and a drop of the liquid to be tested taken up on a glass rod and gently dropped on to the top surface. The liquid will percolate through to the under fold, leaving the precipitate on the upper one. It is then only necessary to unfold the sheet and apply a drop of ferrocyanide to the under surface. If the reaction is complete a faint pink colouration will take place, which is perhaps more easily recognised by transmitted light.

The results obtained by duplicate experiments tend to show that the copper salts are perfectly constant in composition when precipitated in this manner, and the results equal in accuracy any obtained with other processes.

About 1 gm. of barium carbonate was added in each case and the solution

heated up to 90° C. before titration. The temperature at the end of the titration should not be less than 30° C.

The precipitation by copper is done on say 25 c.c. of the solution of the sample and the results noted. 50 c.c. of the same sample are then mixed with the usual proportions of gelatine, salt, acid, and barium sulphate; diluted to 100 c.c., then filtered through a dry filter and 50 c.c. (=25 c.c. of the original liquid) titrated with copper solution as before, the difference being calculated to available tannin.

The experiments show that the separation of the tannic acid by means of an acid solution of gelatine and salt will not affect the general results obtained, and this method for want of a better was used in the experiments, Procter's modification being considered the most accurate, and therefore adopted.

The following table was prepared from experiments, showing the error due to the indicator in c.c. of standard solution added to different quantities of water:—

c.c. of Water.	c.c. of Standard Solution required.
20	0·3
30	0·4
60	0·7
100	1·0
150	1·5

The above correction should be made in all cases.

A sample of so-called pure tannic acid gave the following results:—

Weight taken.	c.c. required.
Gm.	
0·5	25·0
0·5	25·2
0·5	25·2

Slightly lower results were obtained when the operation was conducted in the cold, probably owing to the slower action of the carbonate on the free acid; but the rate of running in of the solution had no appreciable effect on the quantity required.

A sample of the purest gallic acid that could be obtained gave the following figures:—

Weight taken.	c.c. required.
Gm.	
0·5	45·0
0·5	44·8

Allowing that the acid was of 90 per cent. purity, these results would give a value for each c.c. of 0·0111 gm. This figure must of course only be taken as approximate. It will be seen that more solution is required to precipitate the gallic than the tannic acid. This is also noticed in Löwenthal's method.

The chief advantage claimed by the author of this method over Löwenthal's are as follows:—

(1) Both the tannic and gallic acids are determined.
(2) Rapidity where a simple assay is sufficient.

(3) The results are expressed in terms of the copper oxide precipitated.

(4) The standard solution keeps well, and there is no correction necessary for indigo solution or gelatine.

(5) Larger quantities of the solution can be titrated, thus reducing the working error.

It seems to be possible to use this method for substances other than tannic or gallic acids, *e.g.*, Fustic.

The following results were obtained with a sample of pure Fustic extract 51° Tw.

0·5 gm. taken required 11·5 c.c. of standard solution.

0·5 gm. taken required 11·6 c.c. of standard solution.

The end of the reaction was sharp when the titration was carried on at the boiling-point and the precipitate settled well.

Rapid Method for the determination of Tannin Materials.

Gardner and Hodgson* observed that tannic and gallic acids are readily attacked by alkaline reducing agents, and developed the following process for the determination of tannic acid :—

To an aqueous solution of tannic acid standard iodine solution is added in excess, and, after the addition of a few drops of starch solution, sodium hydroxide solution is added until the blue coloration disappears ; an excess of NaOH is to be avoided. Dilute HCl is then added in sufficient amount to liberate the unabsorbed iodine, the amount of which is determined by titration with standard sodium thiosulphate solution. The method was applied to ordinary tannin-containing materials, viz., gall-nuts, sumach, valonia, etc., the results being compared with those obtained by using the Löwenthal process. The difference in the results obtained by the two methods was usually less than 1 per cent. The iodine method was applied both before and after precipitating the tannic acid by means of gelatine, as in the Löwenthal process.

Other Methods of Determining Tannin.

Direct Precipitation by Gelatine.—The difficulty existing with this method is that of getting the precipitate to settle, so that it may be clearly seen when enough gelatine has been added.

Tolerably good results may sometimes be obtained by using a strong solution of sal ammoniac or chrome alum as an adjunct. The best aid is probably barium sulphate, 2 or 3 gm. of which should be added to each portion of liquid used for titration.

Standard solution of gelatine should contain 1·33 gm. of dry gelatine per litre, together with a few drops of chloroform or a small quantity of thymol to preserve it. 45 c.c. = 0·05 gm. tannin (Carles). This method is adapted only for rough technical purposes, as also is the following :—

Direct Precipitation by Antimony.—This method is still in favour with some operators ; but, like the gelatine process, is beset with the difficulty of getting the precipitate to settle.

Standard antimony solution is made by dissolving 2·611 gm. of

* Paper communicated to the seventh International Congress of Applied Chemistry (1909).

crystals of tartar emetic dried at 100° C. in a litre. 1 c.c. = 0·005 gm. tannin. This liquid may also be kept from decomposition by a few grains of thymol. 50 c.c. of the tannin solution may be taken for titration, to which is added 1 or 2 gm. of sal ammoniac, and the antimonial solution run in until no further cloudiness is produced.

In both the above methods the final tests must either be made by repeatedly filtering small portions to ascertain whether the precipitation is complete, or by bringing drops of each liquid together on black glass or a small mirror.

TIN.

Sn = 119.

Metallic iron	× 1·0654 = Tin.
Double iron salt	× 0·1522 = ,,
Factor for $^N/_{10}$ iodine or permanganate solution	0·00595

THE method, originally devised by Streng, for the direct determination of tin by potassium dichromate, or other oxidizing agent in acid solution, has been found most unsatisfactory, from the fact that varying quantities of water or acid seriously interfere with the accuracy of the results. The cause is not fully understood, but that it is owing partly to the oxygen mechanically contained in the water reacting on the very sensitive stannous chloride there can be very little doubt, as the variations are considerably lessened by the use of water recently boiled and cooled in closed vessels. These difficulties are set aside by the processes of Lenssen, Löwenthal, Stromeyer, and others, now to be described, which are found fairly satisfactory.

1. Direct Titration by Iodine in Alkaline Solution. (Lenssen).

Metallic tin or its protosalt, if not already in solution, is dissolved in hydrochloric acid, and a tolerable quantity of Rochelle salt added, together with sodium bicarbonate in excess. If enough tartrate be present, the solution will be clear ; starch is then added, and the mixture titrated with $^N/_{10}$ iodine. Metallic tin is best dissolved in HCl by placing a platinum crucible or cover in contact with it, so as to form a galvanic circuit.

Benas* points out that the chief error in the determination as above arises from oxygen dissolved in the liquid, or absorbed during the operation. In order to obtain constant results, it is necessary to dissolve the tin compound in HCl, dilute with oxygen-free water, and add at once excess of standard iodine, which excess is found by residual titration with standard thiosulphate.

S. W. Young† has called attention to the fact that the determination of tin can be carried out in acid solution, though not in the

* *Chem. Centr-blatt.* **51**, 957. † *J. Am. C. S.* **19**, 809.

same way as advocated by Benas. The solution is best made in dilute hydrochloric acid, and must of course be free from other oxidizing or reducing matters. To prevent the action of air the stannous compound must be rapidly prepared and titrated immediately with excess of standard iodine and starch. It is essential that the potassium iodide used in making the iodine solution should be free from iodate. The determination of the amount of iodine in excess is best done with dilute stannous chloride, the strength of which in relation to the standard iodine must be known either just before or after the tin experiment. The results obtained by Young were a little higher than the theoretical, which is attributed to the iodine being standardized by thiosulphate in a neutral, instead of an acid, solution, but as mentioned in the beginning of this section variations in tin titrations occur from several causes difficult to understand. The method possesses some advantage over the following, inasmuch as iodides, bromides, and salts of iron, when present, cause no difficulty.

2. Indirect Titration by Ferric Chloride and Permanganate (Löwenthal, Stromeyer, etc.).

This method owes its value to the fact that when stannous chloride is brought into contact with ferric or cupric chloride it acts as a reducing agent, in the most exact manner, upon these compounds, stannic chloride being formed, together with a proportionate quantity of ferrous or cuprous salt, as the case may be. If either of the latter be then titrated with permanganate, the original quantity of tin may be found, the reaction being, in the case of iron,—

$$SnCl_2 + Fe_2Cl_6 = SnCl_4 + 2FeCl_2.$$

55·85 iron = 59·5 tin. If decinormal permanganate, or the factor necessary to convert it to that strength, be used, the calculation by means of iron is not necessary.

Method of Procedure: The solution of stannous chloride, or other protosalt of tin in HCl, or the granulated metal, is mixed with pure ferric chloride (which, if tolerably concentrated, dissolves metallic tin readily, and without evolution of hydrogen) then diluted with distilled water, and titrated with permanganate as usual. To obtain the most exact results, it is necessary to make an experiment with the same permanganate upon a like quantity of water, to which ferric chloride is added; the quantity required to produce the same rose colour is deducted from the total permanganate, and the remainder calculated as tin.

Stannic salts, also tin compounds containing iron, are dissolved in water, HCl added, and a plate of clean zinc immersed for ten or twelve hours; the tin so precipitated is carefully collected and washed, then dissolved in HCl, and titrated as above; or the finely divided metal may at once be mixed with an excess of ferric chloride, a little HCl added, and when solution is complete, titrated with permanganate. 4 eq. of iron (=223·4) occurring in the form of ferrous chloride represents 1 eq. (=119) of tin.

Tin may also be precipitated from slightly acid peroxide solution as sulphide by H_2S, the sulphide well washed, and mixed with ferric chloride, the mixture gently warmed, the sulphur filtered off,

and the filtrate then titrated with permanganate as above. 4 eq. of iron = 1 eq. of tin.

Tin Ore.—In the case of analysis of cassiterite, Arnold* recommends that 1 gm. of the very finely powdered mineral be heated to low redness for two hours in a porcelain boat in a glass tube with a brisk current of dry and pure hydrogen gas, by which means the metal is reduced to the metallic state. It is then dissolved in acid ferric chloride, and titrated with permanganate or dichromate in the usual way.

The Determination of Tin in White-metal Alloys. Ibbotson and Brearley.† Tin may readily be determined by reducing the hot solution of the chloride, cooling in an atmosphere of CO_2, and titrating with iodine and starch. The reduction can be conveniently effected by means of iron, but any excess added must be dissolved completely. If antimony is present, it will be precipitated as metal, and cannot be dissolved again, but as cold acid solutions of stannic chloride are not reduced by antimony, which readily reduces them on heating, the solution may be directly titrated with iodine as usual, very good results being obtained. The antimony may be filtered off after the titration and determined, but the results obtained are rather low.

An improvement on the above method consists in reducing the stannic chloride with finely-powdered metallic antimony. The reduction of 0·15 gm. of tin is complete after one minute's boiling, and the excess of antimony which remains undissolved acts as a safeguard during the cooling, since it reduces any tin which may have become oxidized whilst the solution is still hot. Cold solutions of stannous chloride take up oxygen less readily. The test analyses given show that the reduction is complete.

The influence of various substances likely to be present in an ordinary analysis on the above method was examined, and it was found that the presence of iron, chromium, nickel, zinc, manganese, aluminium, bismuth, phosphorus, and sulphur is without effect on the results. The quantity of hydrochloric acid present should always be about one-fifth of the total volume. If copper is present, it will be reduced to the cuprous state, but accurate results may nevertheless be obtained if the iodine is added drop by drop to the vigorously agitated solution, so as to prevent the formation of a local excess of iodine. It is also advisable to have rather more hydrochloric acid present, up to about one-third of the total volume. Cobalt apparently gives very slightly higher values. Lead is without influence if sufficient hydrochloric acid is present to prevent the formation of lead iodide. The presence of arsenic completely vitiates the results, whether the tin is reduced with iron or with antimony. Mercury is reduced to the metallic state, but is not oxidized in cold solutions. If molybdenum or tungsten be present, a coloured lower oxide is formed, but this is not appreciably re-oxidized by the iodine, and the starch blue can be readily distinguished.

* *C. N.* **36**, 238 † *C. N.* **84**, 167.

TITANIUM.

$Ti = 48 \cdot 1$.

H. L. Wells and W. L. Mitchell* allude to a volumetric method of determining titanic acid by Pisani,† which does not appear to have been found satisfactory. Marignac‡ applied Pisani's method to the determination of titanic acid in the presence of niobic acid, special conditions being adopted to avoid the reduction of the latter.

The authors have modified Pisani's process as improved by Marignac, and employ it for the determination of iron together with the titanic acid in ores. Sulphuric acid solutions are used, and the liquid is protected from the air during cooling and titration by means of a current of carbon dioxide.

Method of Procedure: 5 gm. of the pulverized ore are treated with 100 c.c. of concentrated hydrochloric acid in a covered beaker, using a gradually increasing heat, and adding more acid if necessary. When there is no further action, 50 c.c. of a mixture of equal volumes of sulphuric acid and water are added, and the liquid evaporated until it fumes strongly. After cooling, 200 c.c. of water are added, the whole heated until the sulphates dissolve, and the liquid filtered into a litre flask. If anything besides silicious matter is left on the filter-paper, it should be fused with potassium bisulphate, treated with concentrated sulphuric acid, and the sulphates dissolved in hot water and added to the main solution.

The liquid in the flask is made up to the mark with water, and 4 portions of 200 c.c. each taken, 2 in Erlenmeyer flasks (500 c.c.), and the other 2 in ordinary 350 c.c. flasks. Each of these represents 1 gm. of the ore.

To determine the iron, H_2S is passed into the solutions in the ordinary flasks to saturation, after which they are boiled until all the H_2S has been removed, care being taken to avoid any contact of the solution with the air by covering the mouths of the flasks with crucible lids. The flasks are then quickly filled to the neck with cold recently-boiled water, rapidly cooled, transferred to large beakers, and titrated with standard potassium permanganate.

To the solutions in the Erlenmeyer flasks 25 c.c. of concentrated sulphuric acid are added, and 3 or 4 rods of pure zinc, about 50 mm. long and 6 or 7 mm. in diameter are suspended in the liquid by means of a platinum wire attached to the loop of a porcelain crucible lid, which is inverted over the mouth of the flask. The liquid is then gently boiled for 30 or 40 minutes. Then, without interrupting the boiling, a rapid current of CO_2 is introduced under the cover. The flask is now rapidly cooled, the zinc washed with a jet of water and removed, and the solution titrated with permanganate, while the current of CO_2 is still being passed in. The difference between the permanganate used in this case and that required for the iron alone, represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0·7 gives the factor for titanic acid (TiO_2).

The most convenient strength for the permanganate solution is one of 7·9 gm. per litre, corresponding to about 0·014 gm. of metallic iron.

In the determination of iron by reduction with sulphuretted hydrogen, no effect is produced on cold permanganate solution by the precipitated sulphur present, but precipitated sulphides, such as copper sulphide, should be filtered off before boiling.

The results of test analyses of recrystallized potassium titanofluoride (K_2TiF_6) were somewhat low, but probably quite as good or better than any gravimetric method could furnish.

Another method for the determination of titanium and iron in iron, ores, etc. is given by Knecht and Hibbert,|| as follows:—

* *J. Am. C. S.* 1895, 878. † *Compt. Rend.* **59**, 289. ‡ *Z. a. C.* **7**, 112.

|| *New Reduction Methods in Volumetric Analysis* by Knecht and Hibbert, 1910.

Method of Procedure: About 0·5-1·0 gm. of the finely powdered ore is fused with about 10 times its weight of caustic potash in a nickel dish. The melt, when cool, is treated with water, acidified with HCl, and the solution made up to 250 c.c. 25 or 50 c.c. are then transferred to a conical flask (of about 200 c.c. capacity) in which the titanic salt is reduced. The apparatus used is as shown in fig. 55. The flask is fitted with a rubber stopper having 3 holes. The central one carries a glass tube fitted with a Bunsen valve and through it passes a platinum wire carrying a zinc rod *r*. The other two holes are temporarily closed by glass rods. When the titanic solution has been transferred to the flask, HCl is added, and the flask closed by the stopper, and the zinc lowered into the liquid by means of the platinum wire passing through the small pierced rubber stopper, *c*. Reduction will be complete in 15-20 minutes, 20 minutes at least being necessary to ensure complete reduction when much iron is present. One of the glass rods, *a*, is then removed and a stream of carbon dioxide passed into the flask through a tube inserted in the same hole. The zinc is removed from the solution by raising the platinum wire, and the other rod *b* is then removed also. The zinc is washed with a little freshly boiled water from a wash-bottle, the solution cooled, and titrated with *standard iron alum solution*, using potassium sulphocyanate as indicator. The *standard iron alum solution* consists of a solution of about 14 gm. iron alum dissolved in water, acidified with sulphuric acid till the liquid assumes a pale straw colour, and made up to 1 litre. By measuring the exact volume of standard titanous chloride solution (see p. 234) required to reduce 25 c.c. of this iron-alum solution, using potassium sulpho-cyanate as indicator, its strength is determined, and as it will retain the same strength for an indefinite period, this iron alum solution may be used in all subsequent cases for standardizing the titanous chloride solution.

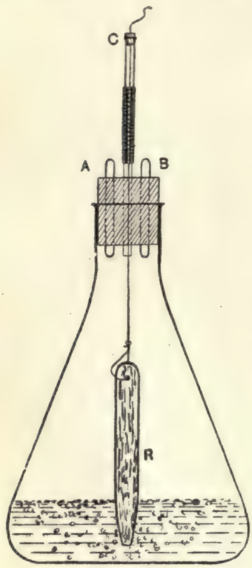


Fig. 55.

Ex. 0·4997 gm. of rutile treated as above and made up to 250 c.c.

25 c.c., after reduction with zinc and hydrochloric acid, required 17·3 c.c. of iron alum solution.

1 c.c. of iron alum solution contained

$$0·001842 \text{ gm. Fe} = \frac{·001842 \times 80·1}{55·85} = 0·002642 \text{ gm. } TiO_2.$$

$$\text{Hence } \frac{·002642 \times 17·3 \times 100}{0·04997} = 91·46\ \%\ TiO_2.$$

Also, 1·960 gm. treated in the same way, and titrated with titanous chloride, required 26·1 c.c.

$$1 \text{ c.c. } TiCl_3 = 0·001432 \text{ gm. Fe} = 0·002047 \text{ gm. } Fe_2O_3.$$

$$\text{Hence } \frac{0·002047 \times 26·1 \times 100}{1·96} = 2·73\ \%\ FeO_3.$$

URANIUM.

U = 238·5.

The determination of uranium may be conducted with great accuracy by permanganate, in precisely the same way as ferrous salts (p. 231). The metal must be in solution either as acetate, sulphate, or chloride, but not as nitrate. In the latter case it is necessary to evaporate to dryness with excess of sulphuric or

hydrochloric acid, or to precipitate with alkali, wash and redissolve in acetic acid.

The reduction to the uranous state is made with zinc, but as the end of reduction cannot, like iron, be known by the colour, it is necessary to continue the action for a certain time; in the case of small quantities for a quarter, of larger for half an hour, at a temperature of 50° to 60° C., and in the presence of excess of sulphuric acid; all the zinc must be dissolved before titration. The solution is then freely diluted with boiled water, sulphuric acid added if necessary, and then permanganate until a faint permanent rose colour is obtained. The ending is distinct if the solution be well diluted, and the reaction is precisely the same as in the case of ferrous salts; namely, 2 eq. of uranium existing in the uranous state require 1 eq. of oxygen to convert them to the uranic state; hence 55·85 Fe = 119·25 U, consequently the strength of any permanganate solution in relation to iron being known, it is easy to find the amount of uranium.

Another method of determining uranium has been published by B. Glasmann.*

The method depends on the reaction of neutral solutions of uranyl salts on a mixture of potassium iodide and iodate—

$$3UO_2(NO_3)_2 + 5KI + KIO_3 + 3H_2O = 3UO_2(OH)_2 + 6KNO_3 + 3I_2.$$

Any excess of acid in the solution must be neutralized with sodium carbonate, which is added till a precipitate begins to be permanent; this precipitate is then just redissolved in dilute acid. Place the solution in a 300 c.c. distillation flask provided with a ground stopper carrying a funnel with stop-cock, the tube of which reaches to the bottom of the flask. Insert the exit tube of the flask into the receiver containing potassium iodide solution, add to the uranyl solution the requisite amount of iodide and iodate mixture, dilute to 120 c.c., close with the stoppered funnel, and slowly heat to boiling. When boiling, cool the receiver with water, and lead a stream of hydrogen through the boiling liquid. When the liquid is reduced to 50 c.c., withdraw the flask from the receiver, remove the burner, wash the delivery tube into a beaker, rinse the contents of the receiver into the same beaker, and titrate with thiosulphate. With 0·2—0·3 gm. of uranyl compound the whole operation requires 20 minutes. The results are accurate, and are not affected by the presence of alkaline-earth chlorides.

VANADIUM.

$V = 51{\cdot}2.$

VANADIUM salts, or the oxides of this element, may be very satisfactorily titrated by reduction with a standard ferrous solution: thus—

$$2FeO + V_2O_5 = Fe_2O_3 + V_2O_4.$$

1 gm. of Fe represents 1·633 gm. of vanadic pentoxide.

Lindemann† recommends the use of a solution of ferrous ammonio-sulphate standardized by $^N/_{10}$ potassium dichromate.

Of course it is necessary that the vanadium compound should be in the highest state of oxidation, preferably in pure sulphuric acid solution. The blue colour of the tetroxide in the dilute liquid has no misleading effect in testing with ferricyanide.

* *Ber.* 1904, 189. † *Z. a. C.* **18**, 99.

With hydrochloric acid great care must be taken to ensure absence of free Cl or other impurities. The end-point in the case of this acid is different from that with sulphuric acid, owing to the colour of the ferric chloride, the mixture becoming clear green.

The accuracy of the action is not interfered with by ferric or chromic salts, alumina, fixed alkalies, or salts of ammonia.

Vanadic solutions being exceedingly sensitive to the action of reducing agents, great care must be exercised to exclude dust or other carbonaceous matters, alcohol, etc.

The reduction of vanadic acid by hydriodic or hydrobromic acid; and its titration in alkaline solution with iodine has been worked out by P. E. Browning.* The solution containing the vanadate is boiled in an Erlenmeyer beaker with potassium iodide or bromide, in not too large a quantity, and a regulated amount of sulphuric acid, until no more iodine or bromine is liberated. After cooling, the residual liquid is nearly neutralized with aqueous potash, a small quantity of tartaric acid is added, and the solution made alkaline by addition of potassium bicarbonate. Excess of standard iodine is then added, and after remaining for half an hour in a well-closed bottle, the free iodine left is determined by means of a solution of arsenious oxide in the usual way.

One mol. of iodine represents 1 mol. of vanadium pentoxide.

Determination of Vanadium (and Chromium) in Steel. The following method† is given by J. Kent Smith, American Vanadium Co., Pittsburg, Pa., U.S.A.

Dissolve 4 grams of the steel in 48 c.c. of water and 12 c.c. of strong sulphuric acid, and when dissolved oxidize with nitric acid, avoiding a great excess. Evaporate to dryness on a hot plate, take up with 150 c.c. of water and boil till dissolved. Add 10 c.c. (or excess) of a $2\frac{1}{2}$ % permanganate solution, and boil for 5 minutes; then add a little manganese sulphate to precipitate any undecomposed permanganate. Cool, dilute to 500 c.c., filter through a dry filter and take 375 c.c. (=3 grams Steel) of the clear filtrate. To this latter add 50 c.c. of dilute sulphuric acid, then a measured excess of $^{N}/_{10}$ ferrous sulphate and titrate back with $^{N}/_{10}$ permanganate till permanently pink: each c.c. of permanganate thus used up equals 0·001743 gm. chromium. Now add 1 or 2 c.c. of ferrous sulphate solution to dissolve any MnO_2 that may have been formed, and add permanganate *very gradually* until the solution is just pink, then cautiously add $^{N}/_{20}$ ferrous sulphate until the pink is just discharged (this should be done exactly to one drop). Next add a carefully measured 5 c.c. (or excess) of $^{N}/_{20}$ ferrous sulphate, and titrate back with $^{N}/_{20}$ dichromate, using potassium ferricyanide as indicator. 1 c.c. $^{N}/_{20}$ dichromate =0·00256 gram Vanadium.

ZINC.

Zn=65·37.

1 c.c. $^{N}/_{10}$ solution=0·003268 gm. Zinc.

Metallic iron	×0·5852	=	Zinc.
,,	×0·7285	=	Zinc oxide.
Double iron salt	×0·0836	=	Zinc.
,, ,,	×0·1041	=	Zinc oxide.

* *J. Amer. Sci.* 1896, 185.

† See Macfarlane's *Laboratory Notes on Iron and Steel Analyses*, p. 222 (1909).

1. Indirect Method (Mann).

THIS process gives exceedingly good results, and consists in precipitating the zinc as hydrated sulphide, decomposing the sulphide with moist silver chloride, then determining the zinc chloride so formed by Volhard's method (p. 145).

The requisite materials are—

Silver chloride.—Well washed and preserved from the light under water.

Standard silver nitrate.—33·006 gm. of pure silver dissolved in nitric acid and made up to 1 litre, or 51·98 gm. silver nitrate per litre. If made direct from silver, the solution must be well boiled to dissipate nitrous acid. 1 c.c. = 0·01 gm. of zinc.

Ammonium thiocyanate.—Of such strength that exactly 3 c.c. suffice to precipitate 1 c.c. of the silver solution.

Ferric indicator and pure nitric acid (see p. 146).

METHOD OF PROCEDURE: 0·5 to 1 gm. of the zinc ore is dissolved in nitric acid. Heavy metals are removed by H_2S, iron and alumina by double precipitation with ammonia. The united filtrates are acidified with acetic acid, and H_2S passed into the liquid until all zinc is precipitated as sulphide. Excess of H_2S is removed by rapid boiling, so that a drop or two of the filtered liquid gives no further stain on lead paper. The precipitate is then allowed to settle, decanted while hot, the precipitate brought on a filter with a little hot water, and, without further washing, the filter with its contents is transferred to a small beaker, 30-50 c.c. of hot water added, well stirred, and so much moist silver chloride added as is judged necessary to decompose the sulphide, leaving an excess of silver. The mixture is now boiled till it shows signs of settling clear; 5 or 6 drops of dilute sulphuric acid (1 : 5) are added to the hot mixture, and in a few minutes the whole of the zinc sulphide will be converted into zinc chloride. The free sulphur and excess of silver chloride are now filtered off, washed, and the chloride in the mixed filtrate and washings determined as follows:—

To the cool liquid, measuring 200 or 300 c.c., are added 5 c.c. of ferric indicator, and so much pure nitric acid as is necessary to remove the yellow colour of the iron. A measured excess of the standard silver solution is then delivered in with the pipette, and without filtering off the silver chloride, or much agitation so as to clot the precipitate, the thiocyanate is cautiously added. with a gentle movement after each addition, until a permanent light brown colour appears.

The volume of silver solution represented by the thiocyanate being deducted from that originally used, will give the volume to be calculated to zinc, each c.c. being equal to 0·01 gm. Zn.

2. Precipitation as Sulphide and subsequent titration with Ferric Salts and Permanganate (Schwarz).

THIS method is based on the fact that when zinc sulphide is mixed with ferric chloride and hydrochloric acid, or better still, with ferric sulphate and sulphuric acid, ferrous or zinc chloride, or sulphate respectively, and free sulphur are produced. If the ferrous salt so produced is determined with permanganate or dichromate, the proportional quantity of zinc present is ascertained. 2 eq. Fe represent 1 eq. Zn.

Preparation of the Ammoniacal Zinc Solution.—In the case of rich ores 1 gm., and poorer qualities 2 gm., of the finely powdered material are put into a small

wide-mouthed flask, and treated with HCl, to which a little nitric acid is added, the mixture is warmed to promote solution, and when this has taken place the excess of acid is evaporated by continued heat. If lead is present, a few drops of concentrated sulphuric acid are added previous to complete dryness, in order to render the lead insoluble; the residue is then extracted with water and filtered. Should metals of the fifth or sixth group be present, they must be removed by H_2S previous to the following treatment. The solution will contain iron, and in some cases manganese. If the iron is not already fully oxidized, the solution must be boiled with nitric acid; if only traces of manganese are present, a few drops of brominated HCl should be added. When cold, the solution may be further diluted if necessary, and then super-saturated with ammonia to precipitate the iron; if the proportion of this metal is small, it will suffice to filter off and wash the oxide with ammoniacal warm water, till the washings give no precipitate of zinc on adding ammonium sulphide. Owing to the fact that this iron precipitate tenaciously holds about a fifth of its weight of zinc, it will be necessary when the proportion is large to redissolve the partly washed precipitate in HCl, and reprecipitate (best as basic acetate); the filtrate from this second precipitate is added to the oringinal zinc filtrate, and the whole made up to a litre.

METHOD OF PROCEDURE: The ammoniacal zinc solution (prepared as described above) is heated, and the zinc precipitated in a tall beaker with a slight excess of sodium or ammonium sulphide, then covered closely with a glass plate, and set aside in a warm place for a few hours. The clear liquid is removed by a siphon, and hot water containing some ammonia again poured over the precipitate, allowed to settle, and again removed, and the washing by decantation repeated three or four times; finally, the precipitate is brought on to a tolerably large and porous filter, and well washed with warm water containing ammonia, till the washings no longer discolour an alkaline lead solution. The filter pump may be used here with great advantage.

The filter with its contents is then pushed through the funnel into a large flask containing a sufficient quantity of ferric sulphate mixed with sulphuric acid, immediately well stoppered or corked, gently shaken, and put into a warm place; after some time it should be again well shaken, and set aside quietly for about ten minutes. After the action is all over the mixture should possess a yellow colour from the presence of undecomposed ferric salt; when the cork or stopper is lifted there should be no odour of H_2S. The flask is then nearly filled with cold distilled water, if necessary some dilute sulphuric acid added, and the contents of the flask titrated with permanganate or dichromate as usual.

The free sulphur and filter will have no reducing effect upon the permanganate if the solution be cool and very dilute.

3. Precipitation by Standard Sodium Sulphide, with Alkaline Lead Solution as Indicator (applicable to most Zinc Ores and Products).

The ammoniacal solution of zinc is prepared just as previously described in Schwarz's method.

Standard sodium sulphide.—A portion of caustic soda solution is saturated with H_2S, sufficient soda added to remove the odour of the free gas, and the whole diluted to a convenient strength for titrating.

Standard zinc solution.—43·993 gm. of pure zinc sulphate are dissolved to the litre. 1 c.c. will then contain 0·01 gm. of metallic zinc, and upon this solution, or one prepared from pure metallic zinc of the same strength, the sulphide solution must be titrated.

Alkaline lead indicator.—Is made by heating together lead

acetate, tartaric acid, and caustic soda solution in excess, until a clear solution is produced. It is preferable to mix the tartaric acid and soda solution first, so as to produce sodium tartrate; or if the latter salt is at hand, it may be used instead of tartaric acid. Some operators use sodium nitroprusside instead of lead.

METHOD OF PROCEDURE: 50 c.c. of zinc solution (=0·5 gm. Zn) are put into a beaker, a mixture of solutions of ammonia and ammonium carbonate (3 of the former to about 1 of the latter) added in sufficient quantity to redissolve the precipitate which first forms. A few drops of the lead solution are then, by means of a glass rod, placed at some distance from each other, on filtering paper, laid upon a slab or plate.

The solution of sodium sulphide contained in an ordinary Mohr's burette is then allowed to flow into the zinc solution until, on bringing a drop from the mixture and placing it upon the filtering paper, so that it may expand and run into a drop of lead solution, a black line appears at the point of contact; the reaction is very delicate. At first it will be difficult, probably, to hit the exact point, but a second trial with 25 or 50 c.c. of zinc solution will enable the operator to be certain of the corresponding strength of the sulphide solution. As this latter is always undergoing a slight change, it is necessary to titrate occasionally.

Direct titration with pure zinc solution gave 99·6 and 100·2, instead of 100.

Groll recommends the use of nickel protochloride as indicator, instead of sodium nitroprusside or lead. The drops are allowed to flow together on a porcelain plate; while the point of contact shows a blue or green colour the zinc is not all precipitated by the sulphide, therefore the latter must be added until a greyish black colour appears at contact.

4. Precipitation as Sulphide with Ferric Indicator (Schaffner).

Schaffner's modification of this process, which is used constantly at the laboratory of the Vieille Montagne and the Rhenish Zinc Works, is conducted as follows:—For ores containing over 35 per cent. zinc, 0·5 gm. is taken; for poorer ones, 1 gm. to 2 gm. Silicates, carbonates, or oxides are treated with hydrochloric acid, adding a small proportion of nitric acid at boiling heat to peroxidize the iron. Sulphur ores are treated with *aqua regia*, evaporated to dryness, and the zinc afterwards extracted by hydrochloric acid; the final ammoniacal solution is then prepared as described on page 371.

METHOD OF PROCEDURE: The titration is made with a solution of sodium sulphide, 1 c.c. of which should equal about 0·01 gm. Zn. The Vieille Montagne laboratory uses ferric chloride as an indicator, according to Schaffner's method. For this purpose a single drop or some few drops of this chloride are let fall into the ammoniacal solution of zinc. The iron which has been added is at once converted into red flakes of hydrated ferric oxide, which sink to the bottom of the flask. If sodium sulphide be dropped from a burette into the solution of zinc, a white precipitate of zinc sulphide is at once thrown down, and the change in the colour of the flakes of ferric hydrate from red to black shows the moment when all the zinc is sulphuretted, and the titration is ended. It is advisable to keep the solution for titration at from 40° to 60° C. Titration carried out under exactly equal conditions, with a known and carefully weighed proportion of zinc,

gives comparative data for calculation, and thus for the determination of the contents of any zinc solution by means of a simple equation. If, for example, 30·45 c.c. of sulphide have been used to precipitate 0·25 gm. of zinc, 1 c.c. of it will precipitate 8·21 mgm. of zinc ($30{\cdot}45 : 0{\cdot}25 = 1 : x$, and therefore $x = 0{\cdot}00821$).

The following method is adopted in the laboratory of a well-known copper works in Wales :—

Reduce the sample to fine powder, and dry at a temperature of about 105° C. Dissolve 0·5 gm. of the sample thus prepared in *aqua regia*, evaporate nearly to dryness, take up with hot water, add 20 c.c. of ammonia and 10 c.c. of a solution of ammonium carbonate (1 to 10), then a few drops of solution of permanganate to precipitate lead and manganese. Now heat nearly to boiling-point and filter into a larger flask, wash the precipitate well with hot water containing ammonia until a drop of the washings shows no reaction with sodium sulphide. The volume of the filtrate and washings should be about 250 c.c., and the temperature about 50° C. Now titrate with a standard solution of sulphide. The most convenient strength is 70 c.c. = 0·5 gm. of pure zinc, heat the sample liquid almost to boiling-point, and add not quite enough sulphide solution to precipitate the whole of the zinc. Now take a drop of a dilute solution of ferric chloride, and let it fall into a small beaker containing a few drops of dilute ammonia, wash the whole contents of the beaker into the assay, and continue titrating slowly and cautiously, at last adding the sulphide solution by 0·1 c.c. at a time, while continually agitating the flask until the ferric oxide at the bottom of the flask begins to turn black, when the assay is finished.

The number of c.c. of sulphide solution used is noted. In order to determine the strength of the sulphide solution, weigh 0·5 gm. pure zinc, place this in a flask, dissolve in 10 c.c. of HCl, and add some hot water, 20 c.c. of ammonia, and 10 c.c. of ammonium carbonate as above, and fill up with hot water to about 250 c.c. Then titrate with the sulphide solution as described. From the number of c.c. used for the 0·5 gm. pure zinc (standard), and the number used for the sample, the zinc contents of the latter can easily be calculated.

The copper present in blendes and calamines does not usually exceed 0·5 per cent. It may be determined colorimetrically, and the amount deducted from the total produced.

If any considerable amount of copper or other impurities be present, they must be separated by the ordinary well-known methods. In order to obtain greater accuracy a correction is made by measuring the volume of the liquid after the assay is finished, and deducting 0·6 c.c. from the sulphide solution used for every 100 c.c. of the volume of the assay : this correction is equally applied to the standard. Experiments have shown that oxide of iron prepared as described above placed in 100 c.c. of distilled water containing ammonia, requires 0·6 c.c. of a sulphide solution of the above strength to turn distinctly black.

The essential point in this volumetric process practised at the Vieille Montagne is the perfect uniformity of working adopted in the assays with reference to the volume of the solutions and reagents used and the colour of the indicator. In titrating, the same quantities of ferric chloride, hydrochloric acid, and ammonia are invariably used. The operation is carried out always at one temperature and in the same time, particularly at the end of the process, when the iron begins to assume that characteristic colour which the flakes show at the edges—points which should not be overlooked. As a further precaution, the titrating apparatus is provided in duplicate, two assays being always made. It permits the execution of several titrations without the necessity of a too frequent renewal of sodium sulphide, which is stored in a yellow flask of large capacity supplying two Mohr's burettes, under

which the beakers can be placed and warmed. A mirror shows by reflection the iron flakes which settle down after shaking the liquid.

Too much stress cannot be laid upon the necessity of standardizing the sodium sulphide under the same conditions as to volume of fluid, proportions of NH_3 and HCl, and colour of the indicator, as will actually be observed in the analysis.

The chief difficulty in this sulphide process is the end-point. E. G. Ballard,* has recommended a good plan for ascertaining this, the following being his own words :—

"I have found the following method very delicate and rapid in determining the end of the titration, and it is based upon the fact that the suspended sulphide of zinc has no action on metallic silver, whereas the smallest excess of sulphide in the solution will produce a stain upon a bright silver surface. A small bright plate of silver is procured, and at intervals during the titration a drop of the zinc solution containing suspended ZnS is taken out on a glass rod and placed upon the silver plate and allowed to remain there for 10 to 20 seconds. No blackening of the silver surface occurs until there is an excess of sulphide present, when the stain upon the silver plate is evident at once, and the titration may be considered finished.

The number of drops of the standard solution of sulphide required to produce the stain in the time mentioned, may be ascertained in a quantity of water equal in bulk to that of the zinc solution operated upon, and afterwards deducted from the total used in calculating the result. One part of Na_2S in 20,000 of water will produce a stain.

Another way to use the silver-plate indicator is to run in the sulphide to small excess, and then titrate back with a solution of zinc of known strength, watching the disappearance of the stain on the silver plate in this instance. Time is thus gained when testing a substance containing an unknown quantity of zinc for the first time, but in cases where the amount is approximately known, the former method suffices, the greater part of the sulphide being run in at once, and the silver-plate indicator applied during the addition of the last portions only.

PRECAUTION : Although it has been stated that the precipitated sulphide of zinc has no action upon the silver plate, yet in the presence of a large excess of ammonia in the cold there is a slight action ; therefore it is desirable to observe the precaution to avoid, as far as possible, adding more ammonia than is required to redissolve the precipitate first formed in rendering the solution of zinc under examination alkaline. However, if the temperature of the solution of zinc be raised to about 180° F., a much larger excess of ammonia may be added without interfering with the accuracy of the test or the final determination of the zinc. Under any circumstances I prefer titrating the solution of zinc hot.

The first appearance of the stain on the silver plate can be more easily distinguished in a diffused light, such as that reflected from a sheet of white paper, or a white card, and more especially if the drop be removed at the end of 10 or 20 seconds by means of a small blotting pad or piece of folded filter-paper.

A porcelain dish is the most convenient vessel in which to perform the titration. Another point to ensure accuracy is to be careful that the silver plate is clean, and free from grease. A little chalk and ammonia is useful for this purpose."

A method of determining zinc by the following means has been found by J. E. Clennell† useful for ores and the solutions used in gold extraction without the use of an external indicator, as is the case with the usual sulphide and ferrocyanide process.

* *J. S. C. I.* **16**, 399. † *C. N.* **87**, 121.

The zinc is precipitated by means of a solution of sodium sulphide of known strength, added in slight excess, the excess of sulphide being then determined by making use of the reaction—

$$Na_2S + 2KAgCy_2 = Ag_2S + 2NaCy + 2KCy.$$

The solutions required are—

Sodium Sulphide.—A convenient strength being about 0·2 per cent. Na_2S.

Silver Double Cyanide.—Prepared by adding silver nitrate to a solution of potassium cyanide (say, 2 or 3 per cent. KCy) till a slight permanent precipitate of AgCy is produced, allowing to stand, and filtering.

Silver Nitrate.—Any dilute solution of known strength. A convenient standard is one containing 5·215 gm. $AgNO_3$ per litre, 1 c.c. being equivalent to 0·001 gm. zinc.

Potassium Iodide.—1 per cent. solution.

It is perhaps advisable also to have a standard zinc solution prepared from pure metallic zinc or pure zinc sulphate, and containing 0·5 or 1 per cent. Zn.

METHOD OF PROCEDURE: The zinc in ores or similar substances is brought into solution in the ordinary way, and the liquid made strongly alkaline with caustic soda or ammonia, boiled, diluted, and filtered if necessary. In cyanide solutions, the sulphide may in general be applied direct; in some cases, however, it may be necessary to remove the cyanogen by a preliminary operation.

The liquid to be examined is mixed with a measured volume of sodium sulphide, slightly in excess of that required to precipitate the whole of the zinc. The liquid is well shaken in a stoppered flask; a little lime may be added to promote settling. The whole, or an aliquot part, is then filtered, and an excess of the double silver cyanide added. The precipitate of Ag_2S generally settles rapidly, and is easily filtered and washed (occasionally it may be necessary to add a little more lime). About 5 c.c. of the 1 per cent. KI solution are added to the filtrate, and the liquid titrated with $AgNO_3$ till a slight yellowish turbidity remains permanent.

$$1 \text{ gm. KCy} = 0{\cdot}3 \text{ gm. } Na_2S = 0{\cdot}25 \text{ gm. Zn.}$$

A table is given which illustrates the results of titrations made by this method with solutions containing known quantities of zinc.

In three trials made with zinc double cyanide, a separate portion of the original liquid was tested in the ordinary way for "total cyanide," *i.e.*, by titration with silver nitrate, using alkali iodide indicator, and the cyanide so found deducted from the amount shown by titration after adding sodium sulphide and the double silver salt. In another test, however, the cyanide was precipitated before making the determination of zinc, by adding excess of $AgNO_3$, and then a few drops of HCl to remove excess of $AgNO_3$, boiling and filtering; making strongly alkaline with NaOH before adding Na_2S.

In presence of ferrocyanide and thiocyanate, it appears to be necessary to make the solution strongly alkaline to ensure complete precipitation of the zinc sulphide.

5. Determination as Ferrocyanide.

In Acetic Acid Solution (Galetti).—When ores containing zinc and iron are dissolved in acid, and the iron precipitated with ammonia, the ferric oxide invariably carries down with it a portion of the zinc, and it is only by repeated precipitation that the complete separation can be made. In this process the zinc is converted into soluble acetate, and titrated by a standard solution of potassium ferrocyanide in the presence of insoluble ferric acetate.

The standard solution of potassium ferrocyanide, as used by Galetti, contains 41·250 gm. per litre. 1 c.c. = 0·01 gm. Zn, but its actual working value must be fixed by experiment.

Standard zinc solution, 10 gm. of pure metallic zinc, dissolved in hydrochloric acid, per litre.

The process is available in the presence of moderate quantities of iron and lead, but copper, manganese, nickel, and cobalt must be absent.

The adjustment of the ferrocyanide solution (which should be freshly prepared at short intervals) must be made in precisely the same way and with the same volume of liquid as the actual analysis of ores, and is best done as follows :—

25 c.c. of zinc solution are measured into a beaker, 15 c.c. of liquid ammonia of sp. gr. 0·900 added to render the solution alkaline, then very cautiously acidified with acetic acid, and 50 c.c. of acid ammonium acetate (made by adding together 20 c.c. of ammonia of sp. gr. 0·900, 15 c.c. of concentrated acetic acid and 65 c.c. of distilled water), which is poured into the mixture, then diluted to 250 c.c., and warmed to about 50° C. The titration is then made with the ferrocyanide solution by adding it from a burette until the whole of the zinc is precipitated. Galetti judges the ending of the process from the first change of colour from white to ash grey, which occurs when the ferrocyanide is in excess ; but it is best to ascertain the ending by taking drops from the solution, and bringing them in contact with solution of uranium acetate on a white plate until a faint brown colour appears. The ferrocyanide solution should be of such strength that measure for measure it agrees with the standard zinc solution.

In examining ores of zinc, such as calamine and blende, Galetti takes 0·5 gm. for the analysis, and makes the solution up to 500 c.c. Calamine is at once treated with HCl in sufficient quantity to bring it into solution. Blende is treated with *aqua regia*, and evaporated with excess of HCl to remove nitric acid. The solutions of zinc so obtained invariably contain iron, which together with the zinc is kept in solution by the HCl, but to ensure the peroxidation of the iron, it is always advisable to add a little potassium chlorate at a boiling heat during the extraction of the ore. The hydrochloric solution is then diluted to about 100 c.c., 30 c.c. of ammonia added, heated to boiling, exactly neutralized with acetic acid, 100 c.c. of the acid ammonium acetate poured in, and diluted to about 500 c.c. The mixture so prepared will contain all the zinc in solution, and the iron will be precipitated as acetate. The titration may at once be proceeded with at a temperature of about 50° to 60° C. by adding the ferrocyanide until the necessary reaction with uranium is obtained. As before mentioned, Galetti takes the change of colour as the ending of the process, and when iron is present this is quite distinguishable, but it requires considerable practice to rely upon, and it is therefore safer to use the uranium indicator. When using the uranium, however, it is better to dilute the zinc solution less, both in the adjustment of the standard ferrocyanide and the analysis of ores. The dilution is necessary with Galetti's method of ending the process, but half the volume of liquid, or even less, is better with the external indicator.

In Hydrochloric Acid Solution (Fahlberg).—This method is not available in the presence of iron, copper, nickel, cobalt, cadmium, lead, or manganese.

Both these processes have been thoroughly investigated by L. de Koninck and E. Prost* with a view to ascertain the exact reactions which take place in adding potassium ferrocyanide to a solution of zinc. The reaction takes place somewhat slowly ; therefore there may, at first, be an excess of ferrocyanide as proved by the uranium reaction. Soon, however, this excess disappears, as an insoluble double compound of zinc and potassium ferrocyanide is formed. The direct titration of zinc by means of potassium ferrocyanide is, therefore, not to be recommended. The following is found by the authors to give trustworthy results.

* *Z. a. C.* 1896, 460, also *C. N.* **76**, 6

METHOD OF PROCEDURE: 10 gm. of pure zinc are dissolved in hydrochloric acid, nearly neutralized with soda, and made up to 1 litre. 27 gm. of potassium ferrocyanide are dissolved in a litre of water. These solutions are then checked by mixing 20 c.c. of the zinc solution with 50 c.c. of a 20 per cent. solution of ammonium chloride, two drops of a 10 per cent. solution of sodium sulphite, and 10 c.c. of hydrochloric acid (sp. gr. 1·075); the zinc solution must be measured from an accurate pipette, but the others are only roughly measured. 40 c.c. exactly of the ferrocyanide solution are now added, and, after being left for at least ten minutes, the excess is titrated with the zinc solution until the uranium reaction is no longer obtained. The relation between the zinc and the ferrocyanide is thus determined.

The determination of zinc in any of its ores is carried out as follows:—2·5 gm. of the sample are dissolved in nitrohydrochloric acid and evaporated to dryness to render any silica insoluble, the residue being taken up with 5 c.c. of hydrochloric acid and a little water. The filtrate from this is freed from lead, cadmium, etc., by a current of hydrogen sulphide, boiled to expel the gas, and, after cooling, mixed with 25 c.c. of saturated bromine water. After pouring the liquid into a 500 c.c. flask, containing 100 c.c. of ammonia (sp. gr. 0·9), and 10 c.c. of a 25 per cent. solution of ammonium bicarbonate, it is, when cold, made up to the mark.

When the precipitate has quite settled, the liquid is passed through a dry filter. 100 c.c. are then pipetted off, acidified with hydrochloric acid, and titrated with the ferrocyanide in the way described.

Maxwell Lyte,* who used the original method of Fahlberg, gives the following method of treating a blende containing lead, copper, and iron in small quantities:—

2 gm. of finely powdered ore were boiled with strong HCl and a little $KClO_3$, the insoluble matter again treated in like manner, the solutions mixed and evaporated somewhat, washed into a beaker, cooled, and moist barium carbonate added to precipitate iron, copper, etc., allowed to stand a few hours, then filtered into a 200 c.c. flask containing 10 c.c. of strong HCl, and washed until the exact measure was obtained. 20 c.c. (=0·2 gm.) of blende were measured into a small beaker, diluted with the same quantity of water, 3 drops of uranic solution added as indicator, and the ferrocyanide delivered in from a burette. When 70 c.c. were added the brown tinge disappeared slowly; the testing on a white plate was then resorted to, and the ferrocyanide added drop by drop, until the proper effect was observed at 73 c.c. As a slight excess of ferrocyanide was necessary to produce the brown colour, 0·2 c.c. was deducted, leaving 72·8 c.c. as the quantity necessary to precipitate all the zinc. The 0·2 gm. of blende therefore contained 0·0728 gm. of Zn or 36·4 per cent.

The sample in question contained about 2·7 per cent. of copper, but this was precipitated with the iron by the barium carbonate; had it contained a larger quantity, the process would not have been available unless the copper was removed by other means.

Mahon† uses the ferrocyanide method much in the same way as above described, but finds that Mn must be absent to ensure good results. In the presence of Mn he separates the Zn from a strong acetic solution with H_2S. The sulphide is then dissolved in HCl and titrated as before.

A modification of the ferrocyanide method so as to be available for the determination of both **zinc and manganese** in the presence of each other has been devised by G. C. Stone.‡

The standard solutions required are:—

Potassium ferrocyanide, about 30 gm. per litre. Its actual working strength is found by titrating it upon a known weight of

* *C. N.* **21**, 222. † *Amer. Chem. Journ.* **4**, 53. ‡ *J. Am. C. S.* **17**, 437.

either zinc or manganese in slightly acid solution, using a very dilute solution of cobalt nitrate as outside indicator. A correction is made in all cases for the amount of ferrocyanide required to give the reaction with the indicator, and may be taken as 0·5 c.c. for every 100 c.c. of the solution titrated.

Potassium permanganate, 1·99 gm. of the pure salt per litre. 1 c.c. = 1 mgm. of Mn.

The end-point of reaction with the indicator is found by placing drops of the cobalt solution on a white tile, and bringing a drop of the liquid under titration in contact with it, but not actually mixing. The immediate production of a faint green line at the junction of the drops is accepted as the correct reading.

METHOD OF PROCEDURE: The ore is dissolved in HCl with the addition of $KClO_3$ as an oxidizer, and care must be taken to have sufficient acid to keep all the manganese in solution.

Lead alone need not be separated; copper can be precipitated by lead; or lead and copper can both be precipitated by aluminium. Cadmium should be precipitated by H_2S, and the filtrate oxidized. Iron and aluminium are best separated by barium carbonate, but the latter must be free from alkali carbonates and hydroxides, barium hydroxide, and ammonium salts. A salt sufficiently pure for the purpose may be obtained by suspending the ordinary pure carbonate (first proved free from ammonium salts) in warm water for several hours with 2 or 3 per cent. of its weight of barium chloride.

The well-oxidized solution of the ore is put into a 500 c.c. flask, and barium carbonate suspended in water added until the precipitate coagulates. The whole is then poured into a beaker, well mixed, allowed to settle, and the clear liquid decanted through a dry filter, and diluted to 500 c.c. Portions of 50, 100 or 200 c.c. of the filtrate are used for each titration. One portion, which should contain between 0·01 and 0·04 gm. of manganese, is diluted to 200 c.c., heated nearly to boiling in a porcelain dish, and titrated rapidly with permanganate with vigorous stirring.

A second portion is made slightly acid with hydrochloric acid, the zinc and manganese are titrated together in the cold with ferrocyanide; the dark colour of the precipitate suddenly changes to light yellowish green shortly before the end of the reaction. It is not necessary to test with the cobalt solution until 1 or 2 c.c. of the ferrocyanide have been added after the lightening of the precipitate.

EXAMPLE: 1 c.c. of the ferrocyanide solution equalled 0·00606 gm. of zinc, or 0·00384 of manganese; 1 c.c. of the permanganate equalled 0·001 gm. of manganese. 2½ gm. of the ore were dissolved, and the iron precipitated and filtered off. 50 c.c. of the solution were diluted, heated, and titrated with permanganate, requiring 18·45 c.c. = 7·38 per cent. of manganese. 100 c.c. titrated with ferrocyanide required 27·85 c.c. of which 9·61 c.c. would be used by the manganese present. Deducting this, 18·24 c.c. was left for the zinc, equal to 0·11053 gm., or 22·11 per cent. The amounts of zinc and manganese as determined gravimetrically were 22·05 and 7·58 per cent. respectively.

Von Schulz and Low's method* as modified by Pattinson and Redpath† (applicable to blende, flue-dust, etc.).

Treat 1 gram of the ore with hydrochloric acid, heat gently, and after some time add nitric acid. Evaporate to dryness, and extract the residue with 1 gram of ammonium chloride and 3—5 c.c. of ammonia; redissolve the residue in hydrochloric acid, evaporate to dryness, and extract a second time, using the same quantities of ammonium chloride and ammonia as before. Filter, and wash

* *J. S. C. I.* 1892, 846. † *J. S. C. I.* 1905, 228.

several times with hot chloride of ammonium solution of 5 % strength. If manganese is present, precipitate it by adding bromine-water to the ammoniacal solution, filter, redissolve the precipitate in hydrochloric acid, add ammonium acetate, precipitate by H_2S any zinc carried down with the manganese, dissolve the ZnS in hydrochloric acid, and add it to the main solution. Add hydrochloric acid till the solution is just acid, then a further 10 c.c. and titrate the solution hot, reserving a portion at first in case two much ferrocyanide should be run in. Use uranium acetate spotted on a white porcelain plate as indicator. (When copper is present, it is removed by Seaman's method, see below).

W. H. Seaman* recommends the use of aluminium (in place of granulated lead previously recommended, which gave rise to high results) for the removal of copper, the process being carried out as follows :—

0·5 gm. of the ore is covered with 7 c.c. of concentrated nitric acid, and an equal volume of hydrochloric acid is then added. The mixture is allowed to act for 15 minutes at a temperature not exceeding 60° C. 7 grams of ammonium chloride are now introduced, and the whole evaporated to dryness. After making alkaline with 5 c.c. of ammonia, 15 c.c. of bromine water are added, and the mixture is boiled for three minutes, filtered hot, and the precipitate washed with a mixture of ammonium chloride and ammonia. The filtrate faintly acidified with hydrochloric acid, is boiled for three minutes with aluminium foil, which precipitates all the copper, lead and cadmium. The foil is then removed, and the liquid titrated hot, the precipitated metals in no way interfering. In standardizing the ferrocyanide solution, the amount of zinc used should correspond as closely as possible to that in the ore, and a correction should always be made for the amount of ferrocyanide required to produce the coloration of the indicator in a blank experiment.

6. Determination as Zinc-Ammonium Phosphate.

The method has been devised by P. H. Walker.† This process is a modification of that devised by Stolba for the determination of magnesium, and is carried out as follows :—

To the zinc solution, which should contain ammonium chloride, a large excess of ammonia is added, then a large excess of sodium phosphate solution. Hydrochloric acid is now gradually added until, after stirring, the solution remains milky, when the liquid is heated to about 75° C., and the gradual addition of acid continued, with constant stirring, until nearly complete neutralization is attained. By this means the precipitate becomes crystalline, and after five minutes' standing it should be filtered off and washed with cold water until the washings show only a faint trace of chloride. The filter paper and precipitate are now returned to the beaker in which the precipitation was carried out, an excess of standard acid added, and the exact point of neutrality determined by means of standard alkali, using methyl orange as indicator. From the equation—

$$ZnNH_4PO_4 + H_2SO_4 = ZnSO_4 + NH_4H_2PO_4$$

it is seen that 1 c.c. of normal acid corresponds with 32·7 mgm. of zinc. The method gives good results. Since the zinc ammonium phosphate is not precipitated in presence of a large excess of ammonia, any magnesium present, which will be precipitated, may be removed by filtration, and the filtrate neutralized to throw down the zinc. Fairly good results are obtained by this method also in the presence of iron, calcium, and magnesium, but any manganese must be previously separated, best by means of nitric acid and potassium chlorate.

* *J. Amer. Chem. Soc.* 1907, 205-211 and *J. S. C. I.* 1907, 258.

† *J. Am. C. S.* 1901, 23, [7], 468—470.

7. Zinc and Lead.

Rupp* has recently devised the following method for the determination of zinc (and lead). It depends on the fact that when a neutral solution of zinc is added to a solution of potassium cyanide the soluble double cyanide $K_2Zn\ (CN)_4$ is formed at first, but the least excess of zinc causes the production of insoluble zinc cyanide. The method is inapplicable in the presence of acetates.

METHOD OF PROCEDURE: The solution of zinc as sulphate or chloride is neutralized by means of caustic soda, using methyl orange as indicator, and made up to a known volume. Into a flask containing about 0·5 gm. of ammonium chloride dissolved in a little water 20 c.c. of $^N/_2$ KCN is accurately measured, and the neutral solution of zinc is run in from a burette into this mixture, with constant agitation, until a permanent turbidity appears. The cyanide solution is standardized in the same way with a solution of pure zinc sulphate. The presence of a salt of ammonia is essential, as it causes the re-solution of precipitate locally formed in the cyanide solution. Too much ammonium chloride causes high results.

1 c.c. $^N/_2$ KCN = 0·008171 gm. Zn.

Lead.—Lead cyanide is not soluble in excess of alkali cyanide, but is readily so in acids. On adding excess of KCN to a lead solution and filtering, the excess of KCN can be titrated with HCl. The solution of lead as nitrate is neutralized by means of NaOH, using methyl orange as indicator, and added to 25 c.c. of $^N/_2$ KCN solution contained in a 100 c.c. measuring flask, the amount of lead present being such that an excess of cyanide remains after it has all been precipitated as $Pb\ (CN)_2$. The flask is made up to the mark, well shaken, allowed to stand for 10 minutes, and filtered. 50 or 75 c.c. of the filtrate are then titrated with $^N/_2$ or $^N/_4$ HCl, using methyl orange as indicator.

1 c.c. $^N/_2$ HCl = 1 c.c. $^N/_2$ KCN = 0·0518 gm. Pb.
1Pb = 2KCN = 2HCl.

The cyanide is standardized by a pure lead salt.

Greenwood and Brislee† consider that of all volumetric processes for the determination of zinc Schaffner's (see p. 373) is of the widest application and affords the highest degree of accuracy. The method was found to give the best results with the assay solution at a temperature between 60° and 80° C., the volume being 150-170 c.c. and containing excess of ammonia. The indicator employed was ferric hydroxide (formed in the assay solution by the addition of 1 drop of a strong solution of ferric chloride), and corrections for the excess volume of liquid and for the excess of sulphide required to blacken the indicator were applied. The ferrocyanide method is recognised as being very rapid and fairly accurate, but in the authors' opinion its value is greatly impaired by the unsatisfactory end-point of the titration when a uranium indicator is employed. Ammonium tetramolybdate is stated to be nearly twice as delicate an indicator as the uranium salt, and its use is recommended for this purpose. Walker's method (see 6) is considered of limited application only, the results being seriously affected in the presence of lime and magnesia.

* *Chem. Zeit.* 1910, **34**, 121.

† The Technical Assay of Zinc, Inst. of Metals, October, 1909, also in *J. S. C. I.*, 1909, 1138.

8. Zinc Dust.

The value of this substance depends upon the amount of metallic zinc contained in it ; but as it generally contains a large proportion of zinc oxide, the foregoing methods are not available for its valuation. The volume of hydrogen yielded by it on treatment with acids appears to be the most accurate, as suggested by Fresenius or by Barnes.* This may very well be done in the nitrometer with decomposing flask, comparing the volume of gas yielded by pure zinc and the sample of dust under examination.

L. de Koninck† has shown that it is necessary to avoid india-rubber connections in the apparatus used, as otherwise there is a loss of hydrogen, due to diffusion.

Many other methods have been proposed for the valuation of this substance. The best is that of Klemp,‡ which consists in treating the dust with an excess of caustic potash and potassium iodate ; the latter is reduced in definite proportion by the metallic zinc to potassium iodide, which is determined by distillation in the iodimetric apparatus, fig. 38 or 39.

The solutions of potash and iodate must be somewhat concentrated, and the mixture with the zinc dust must be intimate, which may be best secured by shaking the whole together in a well-stoppered 200 c.c. flask with glass beads. A 5 per cent. solution of iodate should be used, and the potash solution should be about 40 per cent. For 1 gm. of the dust, 30 c.c. of the iodate and so much of the potash solution should be used as to measure 130 c.c. The weighed substance, together with the beads, being already in the flask, the solutions are added, the stopper greased with vaseline, tied down and shaken for five minutes. then heated on the water-bath, with occasional shaking for one hour. (Digestion without heat gives practically the same results.) The flask is then cooled and the contents diluted to 250 or 500 c.c., and 50 or 100 c.c. placed in the distilling flask, acidified with sulphuric acid, and the iodine so set free distilled into solution of potassium iodide, and titrated with thiosulphate in the usual way. Each gram of iodine equals 1·5451 gm. Zinc.

A simpler method has been devised by A. R. Wahl,|| but like many others it gives no protection against metallic iron, but this of course can be ascertained by other means.

It was found that when solid ferric sulphate is added to zinc dust suspended in a little cold water with exclusion of free acid, a reaction occurs with evolution of heat, and the zinc quickly and totally dissolves with formation of a clear greenish solution. A small residue remains consisting of lead and other impurities. The solution of the zinc takes place without any evolution of hydrogen, and the reaction is therefore represented by the equation—

$$Fe_2(SO_4)_3 + Zn = ZnSO_4 + 2FeSO_4.$$

When all has dissolved, it is only necessary to acidify the solution with sulphuric acid and titrate with permanganate to find the quantity of ferrous salt formed, and hence the quantity of metallic zinc in the sample under examination.

* *J. S. C. I.* **5**, 145. † *J. S. C. I.* 1908, 450.
‡ *Z. a. C.* **29**, 253. || *J. S. C. I.* **16**, 15.

PREPARATION OF PURE FERRIC SULPHATE.—500 gm. of pure ferrous sulphate are dissolved in as little water as possible, and to it are added 100 gm. of sulphuric acid and gradually 210 gm. of nitric acid (60 per cent.). On adding the nitric acid, torrents of nitrous gas are evolved, the solution acquiring a nearly black colour, which disappears again when the whole of the acid is added. The solution is evaporated on the water-bath until it becomes solid, when it is ground with alcohol in a mortar, put on a filter, and washed with alcohol until the filtrate is no longer acid. The product is then dried thoroughly on the water-bath to remove all alcohol, and the salt, which is a perfectly white powder, is kept in stoppered bottles for use.

METHOD OF PROCEDURE: About ½ gm. of zinc dust is put into a stoppered 250 c.c. flask and to it are added 25 c.c. of cold water. The mixture is agitated, and when the zinc is thoroughly suspended, 7 gm. of ferric sulphate are added. There is a gentle evolution of heat, and after shaking for a quarter of an hour the zinc will have completely dissolved, with the exception of a slight residue of impurities. 25 c.c. of strong sulphuric acid are then added, and the flask is made up to the mark with water. 50 c.c. of this solution, after dilution with 50 c.c. of water, are titrated with standard permanganate.

From the quantity of the latter employed, the percentage of metallic zinc is at once found.

Another method is as follows :—*

One gm. of the sample is weighed into a dry stoppered 200 c.c. flask, mixed with 100 c.c. of potassium dichromate solution (30 gm. per litre) and 10 c.c. of 1 : 3 sulphuric acid, and agitated for five minutes. Another 10 c.c. of acid are then added, and the shaking continued for ten or fifteen minutes, when every thing, except a small earthly residue, should be dissolved. The liquid is diluted to 500 c.c., and in 50 c.c. thereof the excess of dichromate is determined by introducing 10 c.c. of 10 per cent. potassium iodide and 5 c.c. of sulphuric acid, titrating the liberated iodine with decinormal thiosulphate.

9. Zinc Oxide and Carbonate.

Benedikt and Cantor† show that zinc oxide and carbonate can be accurately titrated with standard acid and alkali, using methyl orange as indicator; and other zinc salts, using phenolphthalein. The oxide or carbonate is dissolved in excess of acid, and the excess titrated back by soda solution. Zinc salts are dissolved in water (50 c.c. to 0·1 gm. ZnO), phenolphthalein is added, and then standard soda solution to intense red colour. A few more c.c. of soda are then added, the mixture is boiled for some minutes, and the excess of soda titrated. If either free acid or zinc oxide is present in the zinc salt, it is neutralized in presence of methyl orange by alkali or acid, as the case may be.

ACETONE.

Dimethyl-Ketone $CO(CH_3)_2 = 58{\cdot}05$.

ACETONE is an important constituent of wood-spirit and is largely used as a solvent in the manufacture of cordite, the insoluble cellulose hexanitrate being by its aid worked into a homogeneous mixture with the nitroglycerine. For such purposes the acetone must be free from high boiling constituents and especially

* *Analyst* 25, 279. † *Zeit. angew. Chem.* 1888, 236, 237.

from acid or acid-forming substances, which are injurious. The British Government specification* for acetone is as follows :—

"The liquid is to be genuine Acetone and must contain no other ingredients except small quantities of substances which are normal by-products of the manufacture of Acetone. It must be colourless and absolutely transparent, and when mixed with distilled water in any proportions it must show no turbidity. It must leave no residue when evaporated upon a boiling water-bath.

The sp. gr. must not be greater than 0·800 at 15·5° C. compared with water at the same temperature.

One cubic centimetre of a 0·10 per cent. solution in distilled water of pure permanganate of potash added to 100 cubic centimetres of the Acetone must retain its distinctive colour for not less than 30 minutes. This test is to be conducted at a temperature of 15·5° C.

The Acetone is not to contain more than 0·002 per cent. of carbon dioxide, and is otherwise to be quite neutral."

The above stringent requirements ensure that only the middle fractions from the distillation of acetone from acetate of lime are supplied, and that the acetone is not contaminated with foreign matter, and contains no more than traces of any substances except ethyl methyl ketone, and only a small quantity of that.†

Commercial acetones may contain both basic bodies and acids. The basic bodies and strong acids may be determined by diluting a measured volume of the sample with an equal volume of boiled distilled water, adding 2-4 drops of a saturated solution of paranitrophenol in water, and titrating with standard acid or alkali solution. Weak acids may be detected and determined by mixing with water as before, boiling for 5 or 10 minutes, adding phenolphthalein and titrating with standard caustic alkali. Carbon dioxide is readily determined by adding water and phenolphthalein and titrating at once without boiling.

Conroy‡ points out the importance of protecting from light all samples of acetone intended for testing.

Acetone may be determined by Messinger's method,|| which depends upon the fact that when acetone is treated with iodine and potash iodoform and potassium acetate are formed. It is carried out as follows :—

25 c.c. of $^N/_1$ KOH and 1—2 c.c. of the sample (*e.g.*, methyl alcohol) are measured into a stoppered 250 c.c. flask, the mixture well shaken, and allowed to stand for 5 to 10 minutes. $^N/_5$ iodine solution is then run in from a burette, drop by drop, vigorously shaking all the time, until the upper portion of the solution, after standing a minute, becomes quite clear. A few more c.c. of $^N/_5$ iodine are added, as an excess is essential. After shaking, the mixture is allowed to stand for 10—15 minutes and then 25 c.c. $^N/_1$ sulphuric acid are added.

* This was kindly supplied to me by the Director of Artillery, Royal Gunpowder Factory, Waltham Abbey, in June, 1910.—A.E.J.

† Marshall "Acetone: its manufacture and purification," *J. S. C. I.* 1904, **23**, 645.

‡ *J. S. C. I.* 1900, **19**, 209.

|| *Ber.* 1888, **21**, 3666; also *J. S. C. I.* 1889, **8**, 138.

The excess of iodine thus liberated is then titrated with $^N/_{10}$ sodium thiosulphate solution and starch.

Let n be the c.c. of $^N/_5$ iodine required by the acetone (= volume added less half the volume of thiosulphate required), m be the c.c. of sample taken and then

$$\frac{n \times 0{\cdot}19334}{m} = \text{gm. of acetone per 100 c.c.}$$

This includes as acetone any aldehydes, etc., capable of yielding iodoform by this reaction.

ANILINE.

$C_6H_5NH_2 = 93{\cdot}07.$

A PROCESS for determining aniline or its salts has been devised by M. François.* The method depends on the fact that if bromine water is added to an aniline solution, which contains a little soluble indigo as indicator, the bromine does not act on the indigo until all the aniline has been converted into tribromaniline.

METHOD OF PROCEDURE: The bromine water (5 gm. bromine in 1000 c.c. water) is standardized by means of an aqueous solution of aniline hydrochloride, which contains 1·392 gm. of the pure salt in 1000 c.c. (1 c.c. = 0·001 gm. aniline). The bromine water, if exposed to the air, is continually losing bromine; it is therefore essential to use a burette of such capacity that it contains enough bromine water for both the standardization and determination without refilling; to close the end of the burette with a plug of cotton wool; to find approximately the number of c.c. of bromine water required, and then, in the final titration to add nearly the whole at once in order to avoid the slight loss of bromine which occurs when drops of the solution fall through the air. The method may be applied to solutions containing aniline or its hydrochloride, the presence of ammonium chloride does not vitiate the result, and finally, if the solution to be titrated contains mineral substances which would react with the bromine, the aniline may be liberated by potash and distilled in steam. The degree of dilution of the aniline solution does not influence the result.

Another method devised by Reinhardt is described by Liebmann and Studer,† who use a slight modification of it for determining aniline or mixtures of aniline and *o*- and *p*-toluidines which are sometimes present in technical oils. Reinhardt accomplishes this by titration of the oil in hydrobromic acid solution by potassium bromate and bromide.

Aniline requires three molecules of bromine to form tribromo-aniline, whilst *o*- and *p*- toluidine only absorb two molecules.

METHOD OF PROCEDURE: Reinhardt prepares his standard solution by boiling 480 gm. of Br with 336 gm. of KOH (100 per cent.) and 1 litre of water for 2-3 hours, then dilutes to 9 litres.

Hypobromites should not be present.

To carry out the analysis, he dissolves 1·5-2 gm. of oil in 1000 c.c. of water and 100 c.c. of hydrobromic acid of 1·4-1·5 sp. gr. He adds his bromate solution until iodized starch-paper indicates the presence of free bromine.

The following equation gives him the result—

$$X + (VT - X)\,\frac{107}{93}\,\frac{3}{2} = A \text{ or } X = \frac{107}{45}\,VT - \frac{62}{45}\,A,$$

in which X means aniline, V the volume of bromate used, T its titer, and A the

* *J. Pharm.* 1899, 521. † *J. S. C. I.*, 1899, 110.

weight of oil used for analysis. Toluidine is found by difference. To determine the relative quantities of *o*- and *p*-toluidine, use is made of the property of *p*-toluidine and aniline to be precipitated from their hydrochloric acid solution by oxalic acid, whilst *o*-toluidine remains in solution.

160 gm. of the oil are dissolved in 106 gm. of HCl of 20° B, and the mixture is then added to a hot solution of oxalic acid in 10 times its quantity of water.

The solution will at first be clear. It has to stand for 48 hours. The oxalates, which will then have separated out, are filtered and washed three times with 25 c.c. of distilled water.

After decantation with hot dilute KOH (100 c.c. KOH 45° B., 200 c.c. H_2O), the oil is separated, weighed, and finally titrated by the bromine solution to find the amount of *p*-toluidine present.

Liebmann and Studer have adopted this method, with slight modifications, for determining the aniline and toluidine oils, and also for analyzing the aniline salts. To prepare the standard solution, 16·7 gm. of pure potassium bromate and 59·5 gm. of potassium bromide are dissolved in 1 litre of water, and standardized by titration with sodium thiosulphate, using potassium iodide and starch as indicator.

For aniline they have found that concentrated hydrochloric acid can be used as solvent instead of hydrobromic acid, but that the latter is essential when toluidines are present. Instead, however, of using ordinary hydrobromic acid, they found that by dissolving 100 gm. of potassium bromide in 100 c.c. of hot water, and 100 c.c. of hydrochloric acid, sp. gr. 1·18, an acid is obtained which gives accurate results.

For pure aniline 0·5 gm. of the oil, or about 0·6 gm. of salt is dissolved in about 500 c.c. of water and 30 c.c. of pure hydrochloric acid of 1·18 sp. gr., and add the standard solution until a distinct excess of bromine is observable. The reaction grows slower at the end of the operation, but it is found that to wait for two minutes is quite sufficient to determine whether free bromine is present in solution or not. The excess of bromine is determined by titration with $^{N}/_{10}$ thiosulphate solution, using potassium iodide and starch as indicator, 6 c.c. of the thiosulphate corresponding to 1 c.c. of the bromate solution.

For aniline containing toluidine 0·5 gm. is dissolved in 32 c.c. of hydrobromic acid, prepared as above, and 500 c.c. of water, and the titration is carried out in the same way as with pure aniline. A number of analyses of aniline oil and salt and of mixtures of aniline oil with toluidine of known composition gave excellent results.

Another method has been adopted of carrying out Reinhardt's process for determining the aniline and toluidine in aniline oil, which depends on the bromination of these two amines by potassium bromate in hydrobromic acid solution.

An 8 per cent. solution of pure potassium bromate is prepared, the strength being determined by mixing 25 c.c. with 5 gm. of potassium iodide and 3 c.c. of 25 per cent. hydrobromic acid solution, and determining, by titration with standard thiosulphate, the iodine set free according to the equation: $KBrO_3 + 6HBr + 6KI = 3I_2 + 7KBr + 3H_2O$. One gm. of iodine corresponds with 0·21933 gm. of potassium bromate, that is, with 0·12225 gm. of aniline, or 0·1393 gm. of toluidine. About 1 gm. of the aniline oil is dissolved in about 60 gm. of 25 per cent, hydrobromic acid solution, and the bromate solution run in until the clear liquid above the bromide precipitate assumes a yellow coloration. Then, if a is the weight of oil taken, n the number of c.c. of bromate solution employed, t_a and t_t the amounts of aniline and toluidine respectively corresponding with 1 c.c. of the bromate solution, the percentage of aniline in the oil is given by: $100t_a(nt_t - a)/a(t_t - t_a)$, and that of the toluidine by $100t_t(a - nt_a)/a(t_t - t_a)$.

Aniline hydrochloride may be titrated direct by standard caustic alkali, using phenolphthalein or litmus (but not methyl orange) as indicator, as it acts exactly like an equivalent quantity of free

hydrochloric acid. The presence of neutral ammonium salts has no detrimental effect.

AZO-DYES, NITRO- AND NITROSO-COMPOUNDS, Etc.

Dr. E. Knecht's process.

THE powerful reducing properties of titanous chloride ($TiCl_3$) render this reagent capable of being put to a variety of uses in volumetric analysis. Thus, in addition to its uses in the volumetric determination of iron (and arsenic), it has been found available for the exact determination of several series of aromatic compounds, including the azo-compounds, the nitro- and the nitroso-compounds. In all the cases hitherto observed, the reduction takes place in such a manner that each azo-group present requires (in accordance with theory) four equivalents, each nitro group (NO_2) six equivalents, and each nitroso-group (NO) four equivalents of $TiCl_3$. Thus with benzeneazo-betanaphthol, the reaction takes place according to the following equation :—

$$C_6H_5N : N.C_{10}H_6OH + 4TiCl_3 + 4HCl = C_6H_5NH_2 + C_{10}H_6(OH)(NH_2) + 4TiCl_4$$

with picric acid,

$$C_6H_2(OH)(NO_2)_3 + 18TiCl_3 + 18HCl = C_6H_2(OH)(NH_2)_3 + 18TiCl_4 + 12H_2O$$

and with nitrosodimethylaniline,

$$C_6H_4.N(CH_3)_2.NO + 4TiCl_3 + 4HCl = C_6H_4.N(CH_3)_2.NH_2 + 4TiCl_4 + H_2O.$$

In using titanous chloride for these determinations, it is essential that the reagent should be kept out of contact with the air, both in the storage vessel and in the burette, and for this purpose the arrangement shown in fig. 45 should be used.

The most suitable strength of titanous chloride for titrating is a one per cent. solution, obtained by letting down the commercial product with water. For this purpose 50 c.c. of the commercial 20 per cent. solutions are first mixed with an equal volume of strong hydrochloric acid and boiled for a few minutes in a flask. The solution is then made up to a litre with distilled water which has been previously boiled. The method of ascertaining its strength is shown on page 235. When two or more titrations agree, the iron value per c.c. of the titanous chloride solution is easily calculated.

In case the azo-compound under examination is not precipitated by dilute hydrochloric acid, it may be titrated directly, its own intense colour serving as indicator.

For the titrations a solution of 0·5 gm. of the dyestuff made up to 500 c.c. with distilled water, and of this 100 c.c. are taken. The following example may serve as an illustration :—

CRYSTAL SCARLET 6R.—$C_{20}H_{12}N_2S_2O_2Na_2 + 7H_2O$ (colouring matter from alpha naphthylamine and G. salt.)

0·5 gm. of the dyestuff was dissolved in distilled water and the solution made up to 500 c.c. Of this, 100 c.c. were measured out into a conical flask, and after adding about 10 c.c. concentrated hydrochloric acid, boiled for about a minute. This amount required 22·6 c.c. of titanous chloride solution.

The calculation is as follows :—

$$1 \text{ c.c. } TiCl_3 = 0·00158 \text{ gm. Fe}$$

and 502 gm. colour require by theory 224 gm. Fe.

$$\therefore \frac{0·00158 \times 22·6 \times 502}{224} = 0·08002 \text{ gm. colour.}$$

		calc.
and 1 gm. contains 0·8002 or	80·02 %	79·96
Water of cryst. at 140° C. =	19·96	20·04
Total	99·98	100·00

In the case of dyestuffs which, like the majority of the benzidine derivatives, are thrown out of solution by hydrochloric acid, the reaction is too slow and the end of the reaction often not sufficiently sharp to admit of exact determinations. In such cases it is best to run in an excess of titanous chloride solution into the boiling solution of the dyestuff, taking the precaution to keep a gentle current of carbonic acid passing into the flask by a tube which almost touches the surface of the liquid. The reduction will usually be completed in less than two minutes, when the flask is cooled under the tap without, however, interrupting the current of carbonic acid. When cold, the excess of titanous chloride is determined as already described by running in iron alum solution of known strength (but preferably nearly equivalent to that of the titanous chloride solution) until a drop taken out and spotted on potassium sulphocyanide solution just shows a red colour. By subtracting the number of c.c.'s of the iron alum solution (or their equivalent in titanous chloride, should the two solutions not be of equal strength) from the total number of c.c.'s of titanous chloride run in, the exact amount of the latter used up in the reduction of the dyestuff is arrived at.

The following example will serve to illustrate the application of the indirect method :—

Benzopurpurin 4 B, $C_{34}H_{26}N_6S_2O_6K_2 + 4\frac{1}{2}\ H_2O$ (potassium salt of the colouring matter from tolidine and naphthionic acid).

0·5 gm. of the dyestuff is dissolved in distilled water, and the solution made up to 500 c.c. Of this 100 c.c. were measured into a conical flask and heated to the boil. 10 c.c. concentrated hydrochloric acid and 50 c.c. titanous chloride solution were then added, carbonic acid being passed into the flask. The contents of the flask were now boiled for about a minute, when complete reduction took place, and, after cooling, the solution required 22·9 c.c. iron alum (equivalent to 21·0 c.c. titanous chloride). The excess of titanous chloride added was therefore 21·0 c.c., and this, subtracted from 50, gives 29·0 c.c. titanous chloride as having been used for the reduction. The calculation is as follows :—

$$1 \text{ c.c. } TiCl_3 = 0·001845 \text{ gm. Fe}$$

and 756 gm. colour require by theory 448 gm. Fe.

$$\therefore \frac{0·001845 \times 29 \times 756}{448} = 0·09026 \text{ gm. colour.}$$

	Examd.	Calc.
And 1 gm. contains 0·9026 or	90·26 %	90·33 %
Water of cryst	9·63	9·67
	99·89	100·00

For the determination of picric acid and other nitro-compounds, it is also necessary to employ the indirect method, the end of the reaction not being perceptible by the direct method.

CARBON DISULPHIDE AND THIOCARBONATES.

$CS_2 = 76 \cdot 14$.

FOR the purpose of determining carbon disulphide in the air of soils, gases, or in thiocarbonates, Gastine* has devised the following process :—

The gas or vapour to be tested is carefully dried, and then passed through a concentrated solution of recently fused potassium hydroxide in absolute alcohol. The presence of even traces of water seriously diminishes the delicacy of the reaction. The alcoholic solution is afterwards neutralized with acetic acid, diluted with water, and tested for xanthic acid by adding copper sulphate.

In order to determine the distribution of carbon disulphide introduced into the soil, 250 c.c. of the air in the soil is drawn by means of an aspirator through sulphuric acid, and then through bulbs containing the alcoholic potash. For quantitative determinations, a larger quantity of air must be used, and the xanthic acid formed is determined by means of the reaction $2C_3H_6OS_2 + I_2 = 2C_3H_5OS_2 + 2HI$. The alkaline solution is slightly acidified with acetic acid, mixed with excess of sodium bicarbonate, and titrated in the usual way with a solution of iodine, containing 1·68 gm. per litre, 1 c.c. of which is equivalent to 1 mgm. of carbon disulphide.

To apply this method to thiocarbonates, about 1 gm. of the substance, together with about 10 c.c. of water, is introduced into a small flask and decomposed by a solution of zinc or copper sulphate, the flask being heated on a water-bath, and the evolved carbon disulphide passed, first through sulphuric acid and then into alcoholic potash. In the case of gaseous mixtures of carbon disulphide, nitrogen, hydrogen sulphide, carbonic anhydride, carbonic oxide and water vapour the gas is passed through a strong aqueous solution of potash, then into sulphuric acid, and finally into alcoholic potash. The thiocarbonate formed in the first flask is decomposed by treatment with copper or zinc sulphate as above, and the xanthic acid obtained is added to that formed in the third flask, and the whole titrated with iodine.

Harding and Doran's Method.† For CS_2 in Benzene. A known volume of the benzene is shaken in a separating funnel with a solution of potassium hydroxide in absolute alcohol. After standing half an hour, the mixture is extracted several successive times with water containing a little alkali, about 40 c.c. of water and 1 c.c. of alcoholic potassium hydroxide solution being used each time. The aqueous extractions are diluted to a known volume, and a portion is acidified with acetic acid and precipitated by the addition of a distinct excess of standard cupric acetate solution. The precipitate is stirred for about ten minutes, collected on a filter, and washed with four quantities of water, using 15 c.c. each time. About 3 grams of potassium iodide are added to the filtrate, and the liberated iodine is titrated with a sodium thiosulphate solution whose strength in terms of cupric acetate is known. The authors find that the ratio of CuO to CS_2 is 1 to 1·927. This ratio approaches nearest to that between cupric oxide and carbon disulphide in cupric xanthate, which has the formula $(CS.OC_2H_5S)_2Cu$, and in which the ratio is 1 to 1·9126; this tends to strengthen the belief that the compound formed is cupric xanthate.

For CS_2 in Illuminating Gas.—The method consists in passing the gas through a meter, absorbing the carbon dioxide with potassium hydroxide, drying the gas by means of concentrated sulphuric acid, and absorbing the carbon disulphide in an alcoholic solution of potassium hydroxide. The water in the meter must be saturated previously with gas, and about 2 cubic feet of the latter are employed for the determination, the gas being allowed to flow at the rate of 0·5 cubic foot

* *Compt. Rend.* **98**, 1588. † *Journ. Amer. Chem. Soc.* 1907, **29**, 1476.

per hour. The xanthate solution obtained is boiled to expel absorbed gases, cooled, acidified with acetic acid, and precipitated by the addition of standard cupric acetate solution. The determination is then carried out as described above.

FORMALDEHYDE.

$H.CHO = 30{\cdot}02$.

THIS substance is met with in commerce in the form of a 40 % (by volume) aqueous solution ("Formalin") containing usually from 36-38 per cent. by weight of formaldehyde. Solutions containing more than 40 % of formaldehyde polymerise spontaneously to paraformaldehyde.

For the purpose of determining the amounts of formaldehyde in various solutions the following processes are employed :—

LEGLER'S METHOD: 10 c.c. of the solution to be tested are neutralized, if necessary, with $^{N}/_{100}$ soda and placed in a flask, diluted with water, and treated with an excess of standard ammonia solution. The excess is removed by a current of steam and received in standard acid, the result being calculated from the following equation:—$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O$, which represents the reaction which occurs. A small quantity of hexamethylene-tetramine is, however, carried over by the steam. 68·12 parts of ammonia react with 180·12 parts of formaldehyde, or 1 part of ammonia equals 2·6442 parts of formaldehyde. Hexamethylene-tetramine, $N_4(CH_2)_6$, is formed as a condensation product. The action is slow, and according to the experiments of L. F. Kebler* a digestion of 6 hours is necessary in order to get the full proportion of CH_2O. Equally good results were obtained when the mixed solutions were left overnight.

Another method which gives good results is that of Blank and Finkenbeiner.† It is based on the oxidation of formic aldehyde into formic acid by peroxide of hydrogen in alkaline solution, and titration of the excess of alkali.

METHOD OF PROCEDURE: 3 gm. of the solution of formic aldehyde under examination (or 1 gm. in the case of a solid) are weighed out carefully and placed in a tall conical flask containing 25 c.c. of double normal soda (30 c.c. when the concentration of the formic aldehyde is greater than 45 per cent.). The mixture is then immediately treated with 50 c.c. of peroxide of hydrogen at from 2·5 to 3 per cent. strength; in the case of the peroxide having an acid reaction, the acidity should be determined and deducted from the final result. The peroxide of hydrogen must be added gradually (taking about three minutes) by means of a funnel; after two or three minutes the funnel is rinsed with water, and the excess of alkali is titrated with a double normal solution of sulphuric acid; in very exact analyses the water used for rinsing should be boiled first to drive off any carbonic acid. Litmus is used as an indicator.

With solutions containing less than 30 per cent. of formic aldehyde the mixture should be allowed to stand for about ten minutes after the addition of the peroxide of hydrogen, for the reaction to be complete.

The volume of standard alkali used, multiplied by 6, gives the formaldehyde in 1 gm. of the solid or, multiplied by 2, in 3 gm. of the solution.

The reaction takes place with the disengagement of a considerable amount of heat and production of froth.

Experiments on other aldehydes did not give satisfactory results.

A further method, especially applicable to dilute solutions, is furnished by R. Orchard.‡ It is based on the reaction of formaldehyde with ammoniacal silver solution, and in this process

* *Amer. Journ. Pharm.* 1898, 432.

† *Berichte* 1898, 2979, also *Analyst*, 1899, 92.

‡ *Analyst*, 22, 4.

it is arranged quantitatively, and can be carried out either by weight or the residual silver found volumetrically.

METHOD OF PROCEDURE: In the actual experiments 10 c.c. of on approximately 0·1 per cent. solution of formaldehyde were added to 25 c.c. $^N/_{10}$ silver nitrate, 10 c.c. of dilute ammonia (1 of 0·88 solution to 50 of water) added, and the whole boiled in a conical flask attached to a reflux condenser. The precipitate, after filtration and washing, was ignited and weighed as metallic silver, and as a check the excess of silver was determined in the filtrate as silver chloride. As the first experiments showed that the reduction was incomplete after boiling for half an hour, the boiling was continued for four hours. In order to ascertain if any loss took place during boiling, a duplicate determination was made, in which a bottle with a tied-down stopper, heated in a water-bath, was employed. The actual results obtained were in the first case 0·01038 gm. formaldehyde, and in the second 0·0104 gm., consequently there was practically no loss.

In the calculation, as one molecule of CH_2O reduces two molecules of Ag_2O, the weight of the precipitated silver multiplied by the factor 0·0696 gives the weight of the formaldehyde, and 1 c.c. $^N/_{10}$ silver nitrate corresponds to 0·00075 gm. formaldehyde; it is, therefore, possible to determine extremely small quantities by this process.

A number of experiments were carried out on the determination of formaldehyde by G. Romijn.* The methods of Legler, Brochet, and Cambier were studied, and the results obtained with them compared with those given by two new methods described below. For this purpose four aqueous solutions were prepared containing in 500 c.c.: (1) 2·075 gm. of formalin; (2) 2·075 gm. of formalin + 1·3 gm. acetaldehyde; (3) 2·075 gm. of formalin + 0·355 gm. of acetone; (4) 2·075 gm. of formalin + 1 gm. of benzaldehyde.

IODIMETRIC METHOD.—10 c.c. of the aldehyde solution are mixed with 25 c.c. of decinormal iodine solution, and sodium hydrate added drop by drop until the liquid becomes clear yellow. After ten minutes hydrochloric acid is added to liberate the uncombined iodine, which is then titrated back with standard thiosulphate. Two atoms of iodine are equivalent to 1 molecule of formaldehyde. The amount of iodine taken up multiplied by 0·1183 gives the amount of formaldehyde. The results obtained with the first solution showed that the formalin used contained (1) 37·38 and (2) 37·40 per cent. of formaldehyde.

With the second solution a certain amount of iodoform was produced, and the results were too low. With the third solution the acetone was entirely converted to iodoform, and in the fourth solution the benzaldehyde was partially oxidized. Hence this method, though suitable for the valuation of pure formaldehyde, does not give correct results in the presence of other aldehydes.

POTASSIUM CYANIDE METHOD.—This is based on the fact that formaldehyde combines with potassium cyanide. The addition product reduces silver nitrate in the cold. But if the silver nitrate be acidified with nitric acid before the addition of the aldehyde cyanide mixture, no precipitate results if the aldehyde in the latter be in excess. If, on the other hand, the potassium cyanide is in excess, 1 molecule of potassium cyanide is left in combination with 1 molecule of the formaldehyde, while the excess precipitates silver cyanide from the silver nitrate solution.

10 c.c. of decinormal silver nitrate, acidified with nitric acid, are mixed with 10 c.c. of potassium cyanide solution (prepared by dissolving 3·1 gm. of the 96 per cent. salt in 500 c.c.), the whole diluted to 500 c.c., filtered, and 25 c.c. of the filtrate titrated by Volhard's method (p. 145). The difference between this blank result and that obtained by titrating the filtrate after the addition of the aldehyde solution gives the amount of standard sulphocyanide corresponding to the silver not precipitated by the excess of potassium cyanide. From this the amount of formaldehyde can be calculated. With solution 1 the results showed

* *Z. a. C.* 1897, 18–24.

37·39 and 37·67 per cent. of formaldehyde in the formalin. With solution 2, if the titration was made immediately after shaking, only the formaldehyde had combined, but if left for some time the acetaldehyde also began to combine, and erroneous results were obtained. Solutions 3 and 4 gave correct results, even after standing for 30 minutes.

HYDROXYLAMINE METHOD (Brochet and Cambier)*.—This gave satisfactory results with pure formaldehyde, but quite irregular figures with the other three solutions.

LEGLER'S METHOD.†—The four solutions were made more concentrated in order to lessen the difficulty of observing the end-reaction. In each case the correct amount of formaldehyde was found, but the author does not consider the method so accurate as the others.

Acetaldehyde.—A method originally proposed by Reiter‡ has been modified by Roques with good results.

METHOD OF PROCEDURE: A sodium sulphite solution is made by dissolving 12·6 gm. of anhydrous sodium sulphite in 400 c.c. of water, adding 100 c.c. of normal sulphuric acid, diluting to 1000 c.c. with alcohol of 96 %, and filtering after 24 hours. A convenient quantity of the alcoholic solution of aldehyde to be examined is placed in a 100 c.c. stoppered flask, mixed with 50 c.c. of the sulphite solution and made up to 100 c.c. with alcohol of 50 %. A second quantity of 50 c.c. of the sulphite solution is placed in a similar flask, and made up to 100 c.c. with the same alcohol. After heating to 50° C. at least 4 hours, 50 c.c. are withdrawn from each flask, and the sulphurous acid determined by means of $^{N}/_{10}$ iodine solution; the difference is the quantity of sulphurous acid that is in combination with the aldehyde; 1 c.c. of $^{N}/_{10}$ iodine = 0·0022 gm. of aldehyde.

If the liquid to be examined contains less than 1 per cent. of aldehyde the sulphite solution must be diluted; for 0·5 per cent., it should be diluted with an equal volume of alcohol of 50 %, and $^{N}/_{20}$ iodine should be used; for 0·1 per cent., the sulphite should be diluted with alcohol of 50 % to 10 times its ordinary volume, and centinormal iodine solution should be used.

A Volumetric Method for the Determination of various Aldehydes has been devised by M. Ripper.||—The method is based on the combination of alkali bisulphites with aldehydes. 25 c.c. of the solution to be examined, which should not contain more than ½ per cent. of the aldehyde, are run into 50 c.c. of a solution of potassium bisulphite containing 12 gm. $KHSO_3$ per litre, placed in a 150 c.c. flask, which is then securely corked, and allowed to stand for a quarter of an hour. During this time another 50 c.c. of the potassium bisulphite solution are titrated with $^{N}/_{10}$ iodine. The excess of bisulphite added to the aldehyde solution is then determined with the same iodine solution, and from the difference the amount of aldehyde present is calculated.

The amount of the aldehyde is obtained by the formula—

$$A = \frac{I \times \frac{M}{2}}{126·92} = \frac{I \times M}{253·84}$$

in which A represents the amount of aldehyde, I the iodine corresponding to the combined sulphurous acid, and M the molecular weight of the aldehyde in question.

From this the following factors are obtained:—

Formaldehyde $= I \times 0·1179$.
Acetaldehyde $= I \times 0·1729$
Benzaldehyde $= I \times 0·4166$
Vanillin $= I \times 0·5974$.

* *Comp. Rend.* 120, 449. † *Ber.* 16, 1335. ‡ *J. S. C. I. abstr.* 1897, 606.
|| *Monatshefte f. Chem.* 21, 1079.

The method is said to yield reliable results in all cases in which the aldehyde is soluble in water, or can be brought into solution by the addition of a little alcohol.

In the case of the four aldehydes mentioned above, test analyses are described in detail to show that the results are in close agreement with those obtained by recognised reliable methods.

Solutions of potassium bisulphite stronger than the above should not be employed, as the larger quantities of hydriodic acid formed would exert a reducing action on the sulphuric acid formed. The use of alcohol to dissolve the aldehyde should also be avoided as far as possible, as even relatively small quantities of alcohol (upwards of 5 per cent.) interfere with the iodide of starch reaction. With the very dilute solutions of aldehyde used, however, a very small addition of alcohol will be sufficient in most cases.

GLYCEROL.

GLYCERIN.

$$C_3H_5(OH)_3=92{\cdot}06.$$

UP to a recent time no satisfactory method of determining glycerin had been devised, but the problem has now been solved in a tolerably satisfactory manner. The permanganate method of oxidation appears to have been originally suggested by Wanklyn, improved by him and Fox, and further elaborated by Benedikt and Zsigmondy.* With fatty matters it depends on the saponification of the fat, and oxidation of the resultant glycerol by permanganate in alkaline solution, with formation of oxalic acid, carbon dioxide, and water, thus—

$$C_3H_8O_3+3O_2=C_2H_2O_4+CO_2+3H_2O.$$

Aqueous solutions of glycerin may of course be submitted to the method very easily.

The excess of permanganate is destroyed by a sulphite, the liquid filtered from the manganese precipitate, the oxalic acid then precipitated by a soluble calcium salt in acetic solution, and the precipitated calcium oxalate, after ignition to convert it into carbonate, titrated with standard acid in the usual way, or the oxalic precipitate titrated with permanganate. The oxalic solution may be titrated direct after addition of H_2SO_4 with permanganate; but Allen and Belcher have found this method faulty, probably from the formation of a dithionate, due to the sulphite. On the other hand, they have obtained very satisfactory results by the alkalimetric or the permanganate titration on known weights of pure oxalic acid and glycerin.

These operators have also shown that, in the case of dealing with fats, where it has been recommended by Wanklyn and Fox to use ordinary alcohol as the solvent, and by Benedikt methyl alcohol, both these media, especially ethylic alcohol, themselves produce a variable quantity of oxalic acid when treated with alkaline permanganate, and hence vitiate the process. Again, if

* *Chem. Zeit.* **9**, 975, and *J. S. C. I.* 1885 610.

it be attempted to avoid this by boiling off the alcohols, there is a danger of losing glycerin.*

Allen's method† with oils and fats is as follows :—

10 gm. of the fat or oil are placed in a strong small bottle, together with 4 gm. of pure KHO dissolved in 25 c.c. of water. A solid rubber stopper is then used to close the bottle, and tied down firmly with wire. It is then placed in boiling water, or in a water oven, and heated, with occasional shaking, from 6 to 10 hours, or until the contents are homogeneous, and all oily globules have disappeared. When saponification is complete, the bottle is emptied into a beaker and diluted with hot water which should give a clear solution, the fatty acids are then separated by dilute acid, filtered, and the filtrate made up to a given volume.

This solution, which will usually contain from 0·2 to 0·5 gm. of glycerol, according to its origin, is transferred to a porcelain basin and diluted with cold water to about 400 c.c. From 10 to 12 gm. of caustic potash should next be added, and then a saturated aqueous solution of potassium permanganate until the liquid is no longer green but blue or blackish. An excess does no harm. The liquid is then heated and boiled for about an hour, when a strong solution of sodium sulphite should be added, drop by drop, to the boiling liquid until it just becomes colourless. The liquid containing the precipitated oxide of manganese is then poured into a 500 c.c. flask, and hot water added to 15 c.c. above the mark, the excess being an allowance for the volume of the precipitate and for the increased measure of the hot liquid. The solution is then passed through a dry filter, and, when cool, 400 c.c. of the filtrate should be measured off, acidified with acetic acid, and precipitated with calcium chloride. The solution is kept warm for three hours, or until the deposition of the calcium oxalate is complete, and is then filtered, the precipitate being washed with hot water. The precipitate consists mainly of calcium oxalate, but is liable to be contaminated more or less with calcium sulphate, silicate, and other impurities, and hence should not be directly weighed. It may be ignited, and the amount of oxalate previously present deduced from the volume of normal acid neutralized by the residual calcium carbonate, but a preferable plan is to titrate the oxalate by standard permanganate. For this purpose, the filter should be pierced and the precipitate rinsed into a porcelain basin. The neck of the funnel is then plugged, and the filter filled with dilute sulphuric acid. After standing for five or ten minutes this is allowed to run into the basin and the filter washed with water. Acid is added to the contents of the basin in quantity sufficient to bring the total amount used to 10 c.c. of concentrated acid, the liquid diluted to about 200 c.c., brought to a temperature of about 60° C., and decinormal permanganate added gradually till a distinct pink colouration remains after stirring. Each c.c. of permanganate used corresponds to 0·0045 gm. of anhydrous oxalic acid, or to 0·0046 gm. of glycerol. Operating in the way described, the volume of permanganate solution required will generally range between 70 and 100 c.c.

C. Mangold‡ advocates the reduction of the excess of permanganate by hydrogen peroxide in preference to sodium sulphite as used by Allen. The author simplifies the method by carrying out the oxidation in the cold.

METHOD OF PROCEDURE : 2-4 gm. of fat are saponified ; the filtrate from the liberated fatty acids is put into a litre flask, diluted to 300 c.c., 10 gm. potassium hydroxide added, and as much of a 5 per cent. permanganate solution as will correspond to $1\frac{1}{2}$ times the theoretical quantity required for the oxidation of the glycerol (1 gm. $C_3H_8O_3$ theoretically requires 6·87 gm. $KMnO_4$). The operation is conducted in the cold and with constant shaking. The mixture is allowed to stand at the ordinary temperature for half an hour. Hydrogen peroxide

* In dealing with waxes or similar bodies including sperm oil, potash dissolved in methyl alcohol must be used for the saponification, as it is almost impossible to saponify with aqueous potash.

† *Commercial Org. Analysis*, 2, 290.

‡ *Zeit. f. angew. Chem.* 1891, 400.

is then added (avoiding, however, a large excess) until the liquid becomes colourless. Then make up to 1000 c.c., shake well, and filter off 500 c.c. through a dry filter. Boil the filtrate for half an hour to decompose all hydrogen peroxide, allow to cool to 60° C., acidify with sulphuric acid, and titrate with standard permanganate solution.

Otto Hehner* has experimented largely on the determination of glycerol in soap lyes and crude glycerins. The volumetric methods recommended in preference to the permanganate are oxidation with potassium dichromate, or conversion of the glycerol into triacetin.

The Dichromate Method.—One part of glycerol is quantitatively oxidized to carbonic acid by 7·486 parts of dichromate in the presence of sulphuric acid. The solutions required are :—

Standard potassium dichromate.—74·86 gm. of pure potassium dichromate are dissolved in water. 150 c.c. of concentrated sulphuric acid added, and when cold diluted to a litre. 1 c.c. =0·01 gm. glycerol.

A weaker solution is also made by diluting 100 c.c. of the strong solution to a litre.

These solutions should be controlled by a ferrous solution of known strength, if there is any doubt about the purity of the dichromate.

Solution of double iron salt.—240 gm. of ferrous ammonium sulphate are dissolved with 50 c.c. of concentrated sulphuric acid to a litre, and its relation to the standard dichromate must be accurately found from time to time by titration with the latter, using the ferricyanide indicator (p. 126).

Method of Procedure: With concentrated or tolerably pure samples of glycerin it is only necessary to take a small weighed portion, say 0·2 gm. or so, dilute moderately, add 10 or 15 c.c. of concentrated sulphuric acid and 30 or 40 c.c. of the stronger dichromate, place the beaker covered with a watch glass in a water-bath and digest for two hours; the excess of dichromate is then found by titration with the standard iron solution. The weaker dichromate is useful in completing the titration where accuracy is required. As the stronger dichromate and the iron solution are both concentrated, they must be used at a temperature as near 15° C. as possible. If the operation be carried out on a water-bath and kept at normal temperature during the operation no correction will be necessary. In the case of crude glycerin it must be purified from chlorine or aldehyde compounds as follows:—About 1·5 gm. of the diluted sample is placed in a 100 c.c. flask, some moist silver oxide added, and allowed to stand 10 minutes. Basic lead acetate is then added in slight excess, the measure made up to 100 c.c., filtered through a dry filter, and 25 c.c. or so digested with excess of dichromate, and titrated as before described.

Richardson and Jaffé† have published a modification of this method for the treatment of crude glycerins.

Method of Procedure: 25 gm. of the samples are made up with water to 50 c.c. of solution, and of this 25 c.c. are taken, and precipitated with 7 c.c. of the official solution of basic acetate of lead (Liquor Plumbi Subacetatis B.P.). The mixture is filtered through a Swedish filter into a 250 c.c. flask. Repeated washings are made with about 150 c.c. of cold water. The excess of lead (which

* *J. S. C. I.* 8, 4. † *J. S. C. I.* 1898, 330.

should be small) is precipitated by an excess of dilute sulphuric acid. After making to the mark and shaking, the liquid is poured on to a dry Swedish filter, 20 c.c. of the filtrate (representing 2 gm. of the original sample of crude glycerin) are pipetted into a beaker, the mouth of which is closed by a funnel with short stem; then 25 c.c. of Hehner's strong standard dichromate solution are added; finally 25 c.c. of pure sulphuric acid are cautiously mixed with the other fluids. After 20 minutes' heating in a water-bath, the oxidation is complete. After cooling, the liquid is made to 250 c.c. with water, and this solution is then titrated upon 20 c.c. of a solution containing 2·982 per cent. of the double sulphate of iron and ammonia, using ferricyanide of potassium to determine the end-reaction in the usual manner.

The portion of the iron solution taken represents 0·01 gm. of glycerin; therefore, if A is the number of c.c. of the dichromate mixture required, and x the percentage of glycerin sought, we have the simple formula—

$$x = (0{\cdot}25 - \frac{250}{A} \times 0{\cdot}01) \times 500$$

(0·25 gm. is the equivalent of glycerin represented by that 25 c.c. of dichromate used, containing 74·86 gm. per litre).

In the case of a spent lye we take 2·5 gm. and dilute to 50 c.c.; the precipitation of chlorides and organic impurities is effected by the addition of a slight excess of the solution of basic lead acetate, and the operation proceeds as in the case of the crude glycerin, with the exception that the lead sulphate is filtered off and the filtrate is concentrated to about 25 c.c. before the addition of the dichromate and the sulphuric acid is made.

The Acetin Method.—This process is based on the quantitative conversion of glycerol into triacetin by heating concentrated glycerol with acetic anhydride, the reaction being

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Acetic anhydride.}}{3(C_2H_3O)_2O} = \underset{\text{Triacetin.}}{C_3H_5(O.C_2H_3O)_3} + \underset{\text{Acetic acid.}}{3C_2H_4O_2}.$$

If the product of this reaction is then dissolved in water, and the free acetic acid neutralized, the dissolved triacetin can easily be determined by saponifying with a known volume of standard alkali and titrating back.

It is due to Benedikt and Cantor,* and recommends itself by its simplicity and rapidity as compared with other methods. Hehner has pointed out the precautions necessary to ensure accuracy as follows:—

Method of Procedure: About 1·5 gm. of the crude glycerin, accurately weighed, is placed in a round-bottomed flask holding about 100 c.c., together with 7 gm. of acetic anhydride and 3 gm. of perfectly anhydrous sodium acetate; an upright condenser is attached to the flask, and the contents are heated to gentle boiling for one hour and a half. After cooling a little, 50 c.c. of warm water are added through the tube of the condenser, and the mixture heated, but not boiled, until all triacetin has, by shaking, dissolved. As triacetin is volatile with water vapour, these operations should be conducted whilst the flask is still connected with the condenser. The solution is then filtered into a large flask (500—600 c.c.), the residue or filter well washed, the liquid *allowed to cool down* to the ordinary temperature, some phenolphthalein added, and the acidity exactly neutralized by a dilute solution of caustic soda; whilst running in the soda the liquid must be shaken continually to prevent local excess of the alkali. The neutral point is reached when the slightly yellowish colour is just changed to reddish-yellow. It must not become pink or the test is spoiled, as the excess of soda cannot be titrated back owing to any excess of alkali saponifying a portion of the acetin.

* *Monatsheft* **9**, 521.

The triacetin is then saponified by adding 25 c.c. of an approximately 10 per cent. solution of pure caustic soda standardized with normal sulphuric or hydrochloric acid, and boiling for 10 minutes, taking care to attach a reflux condenser to the flask. The excess of alkali is then titrated back with normal acid, each c.c. of which represents 0·03067 gm. of glycerol.

It is essential that the processes of analysis should be rapid and continuous, and especially that the free acetic acid in the first process be neutralized very cautiously, and with constant agitation to avoid the local action of alkali.

EXAMPLE.—1·324 gm. of a sample were treated as above. 25 c.c. of the strong soda solution required 60·5 c.c. of normal hydrochloric acid, and 21·5 c.c. were required for titrating back.

Hence $60{\cdot}5 - 21{\cdot}5 = 39{\cdot}0$ c.c. had been used, and the sample contained $39 \times 0{\cdot}03067 = 1{\cdot}196$ gm. or 90·3 per cent. of glycerol.

Weak soap lyes should be concentrated to 50 per cent. of glycerin if determined by the acetin method ; if not the dichromate method must be used.

For fats and soaps about 3 gm. should be saponified with alcoholic potash, diluted with 200 c.c. of water, the fatty acids separated and filtered off. The filtrate and washings are then rapidly boiled to one half and titrated with dichromate.

In the case of crude glycerins the permanganate method is not so reliable as the acetin or dichromate method, owing probably to the oxidation of foreign matters into oxalates. Hehner has shown by comparative experiments with both acetin and dichromate methods that the results agree well, and the same has been verified by Lewkowitsch.

The latter authority has called attention to the difficulties which occur in examining crude lyes for glycerol at the present time owing to the very impure fats used in soap making, etc.* The dichromate method is liable to produce very high results. The acetin process is only applicable to strong lyes containing not less than about 60 per cent. of glycerol and cannot therefore be used with weak lyes. The best method is therefore to take, say, 1000 gm. or c.c., purify the lye and concentrate down so as to prepare a crude glycerin in which the glycerol may be determined by the acetin method.

INDIGO.

(Indigotin $C_{16}H_{10}N_2O_2$.)

THE valuation of indigo for its real dyeing property has created for many years past a large number of chemical processes, but those which give anything like reliable results seem to necessitate an enormous amount of time and care, together with very complicated forms of apparatus, the use of which, successfully, requires the purification of the commercial material from various accompanying substances in order to get satisfactory results.

One of the earliest methods used was the permanganate test, but owing to the presence of other substances in the natural product

* *Analyst* 28, 104.

which affected the test as though they were true indigotin it ceased to command much confidence.

Longer experience and the discovery of methods for purifying the raw material have, however, overcome the former difficulty to a great extent, and C. Rawson* has contributed to various journals improved permanganate methods. In the first communication the oxidation of sulphindigotic acid by permanganate is described as follows :—

METHOD OF PROCEDURE: To obtain a solution of sulphindigotic acid, 1 gm. of finely-powdered indigo is intimately mixed in a small mortar with its own weight of ground glass. The mixture is gradually and carefully added during constant stirring with a glass rod to 20 c.c. of concentrated H_2SO_4 (sp. gr. 1·845) contained in a cylindrical porcelain crucible (cap. 50 c.c.); the mortar is rinsed out with a little powdered glass, which is added to the contents of the crucible, and the whole is exposed in a steam-oven for a period of one hour to a temperature of 90° C. The sulphindigotic acid thus formed is diluted with water and made up to a litre. The solution must be filtered, in order to separate certain insoluble impurities, which otherwise would interfere with the subsequent operations. 50 c.c. of the clear solution are measured into a porcelain dish, to which are added 250 c.c. of distilled water. To this diluted liquid a solution of potassium permanganate (0·5 gm. per litre) is gradually run in from a burette until the liquid, which at first has a greenish tint, changes to a light yellow, the sulphindigotic acid being converted by oxidation into a yellow body named sulphiatic acid. It would appear that indigo-red acts upon permanganate in the same way as indigotin, whereas indigo-brown is precipitated from its solution in strong H_2SO_4 on diluting, and does not affect the result; but indigo-gluten and the mineral portion strongly decolourize permanganate. As indigo-red cannot be regarded as an impurity, the inaccuracy in the analysis may be chiefly ascribed to the gluten and mineral impurities. To eliminate this source of error, the author makes use of the property of sodium sulphindigotate of being almost insoluble in solutions of common salt. The 50 c.c. of the filtered solution of indigo instead of being directly titrated with permanganate, are mixed in a small flask with 50 c.c. of water and 32 gm. of common salt. The liquid, which is almost saturated with the salt, is allowed to stand for two hours, when it is filtered, and the precipitate washed with about 50 c.c. of a solution of salt (sp. gr. 1·2). The precipitated sulphindigotate of soda is dissolved in hot water, the solution is cooled, mixed with 1 c.c. sulphuric acid and diluted to 300 c.c. The liquid is then titrated with potassium permanganate as before. A small correction is necessary owing to the slight solubility of the sodium sulphindigotate in the salt solution. For 0·05 gm. of the indigo sample 0·0008 gm. must be added to the amount of indigotin found.

In the later contribution, C. Rawson gives a new method for removal of impurities from indigo solutions previous to testing, which answers well for technical purposes and is described as follows :—

When commercial indigo is dissolved in concentrated sulphuric acid and the liquid diluted with water, the colouring matter remains in solution as a disulphonic acid, and various impurities are held in suspension. Before proceeding further with the testing it is necessary to remove the suspended matter, and this is usually done by filtration. Filter-paper abstracts some of the colouring matter, and on this account the first portions coming through are rejected in the same way as in testing tannins. Some qualities of filter-paper abstract more colouring matter than others, and the rate of filtration also causes a difference.

Moreover, some of the suspended impurities are in an exceedingly fine state of division, and are liable to pass through many kinds of filter-paper, and thus lead

* *Journ. Soc. Dyers and Colourists*, 1885, 74; and *J. S. C. I.* 1899, 251.

to inaccurate results. In order to avoid these sources of error, a number of tests were made with solutions where the impurities were allowed to subside, but it was found that with some classes of indigo, subsidence was not complete after many hours. Various precipitants were then tried and barium chloride was found to give most satisfactory results. The proportions recommended are as follows :—

METHOD OF PROCEDURE : 0·5 gm. of powdered indigo mixed with glass powder is digested with 25 c.c. pure concentrated sulphuric acid at a temperature of 70° C. for an hour. When cold, the liquid is diluted with water, mixed with 10 c.c. of a 20 per cent. solution of barium chloride and made up to 500 c.c. In 15 to 20 minutes the barium sulphate formed, carrying down with it all suspended impurities, will have settled, and the requisite amount of perfectly clear solution may be withdrawn by a pipette for titration. By this means not only are the results more concordant, but the solution is clearer, than when filter-paper is used. In fact, the results thus obtained are practically the same as those given by "salting out." Tests made with pure indigotin show that no colouring matter is precipitated by the barium chloride.

Rawson lays special stress on the importance of using *pure* sulphuric acid for dissolving the indigo. It should contain not less than 97 per cent. of H_2SO_4, and should be quite free from nitrogen acids and sulphurous acid.

With indigo containing more than 1 or 2 per cent. of indirubin (or red indigo), the ordinary methods of analysis suitable for determining indigotin are not applicable. Very good results may be obtained by a colorimetric method. For this purpose the following is recommended :—

From 0·1 to 0·25 gm. of the finely powdered sample is boiled with about 150 c.c. of ether for half an hour in a flask attached to an inverted condenser. When cold, the solution is made up to 200 c.c. with ether and mixed with 10 c.c. of water in a bottle. Shaking up with a little water causes the suspended particles of indigo to settle immediately, and a clear solution of indirubin is at once obtained without filtering. A measured quantity of the solution is withdrawn and compared in a colorimeter with a standard solution of indirubin. The proportion of ether recommended may seem large, but although pure indirubin is freely soluble in ether, it is by no means readily extracted from indigo.

For the determination of indigotin in indigo rich in indirubin, it is advisable to boil up repeatedly with alcohol, and collect on an asbestos filter.

Indirubin may also be conveniently removed by boiling with glacial acetic acid, as recommended by W. F. Kopperschaar.

In view of the difficulties attending the separation of pure indigotin and indirubin from the other constituents of indigo, and the possible presence of substances similar to the yellow body described,* perhaps the best general commercial method of examination will be found to be one based on colorimetry. For

* In this second paper Rawson describes the existence of a yellow compound found in Java indigo, amounting in some cases to 20 per cent., and the existence of which interferes with any of the ordinary technical processes of analysis used for indigo. It may be discovered by adding a solution of caustic soda or ammonia to the powdered indigo in a white basin or on filter-paper. If present the alkali produces a deep yellow colour. In cases where this occurs it must be removed by boiling the weighed sample of indigo in alcohol and the indigo collected on an asbestos filter, washed with alcohol and dried before being converted into sulphindigotic acid. It must be borne in mind, however, that the boiling with alcohol also removes indirubin.

this purpose, in order that indigotin and indirubin may be determined at the same time, a good and delicate colorimeter in conjunction with Lovibond's tintometer is a desideratum. The relation between the standard permanganate used and indigotin is best established upon the purest indigotin obtainable.

A much more troublesome method, but one which is believed to give the most accurate results, is one originated by Müller and further improved by Bernthsen.* The apparatus used is complicated, and is practically on the same principle as that described for determining oxygen in waters and figured here on page 293. A somewhat simpler arrangement for indigo is described by B. W. Gerland,† it is, in fact, the same apparatus as was used by Tiemann and Preuss‡ for determination of oxygen in waters, but even with this method commercial indigo cannot be successfully tested without previous troublesome purification, and is therefore hardly a suitable substance for technical examinations.

OILS, FATS, AND WAXES.

UNDER the terms oils, fats, and waxes (liquid and solid) are comprised all those naturally-formed substances, derived from both the vegetable and the animal kingdoms, which consist mostly of glyceryl or other esters of the higher members of the several series of fatty or aliphatic acids, with which in some cases notable amounts of the free fatty acids and of the free alcohols themselves are admixed. The term wax is also used to designate certain solid hydrocarbons, the mineral waxes (*e.g.*, paraffin wax, ozokerite).

In the examination of the above as to their identity and for the detection of adulteration, valuable aid is lent by physical methods of examination, such as specific gravity, refractive index, rotatory power, etc., for an account of which other works must be consulted. The chemical methods of examination are based on the determination of "values," which furnish a measure of the quantity of the acids, alcohols, etc., present in the sample examined, without, however, fixing their absolute quantity. In order to secure comparable results, it is absolutely essential to adhere strictly to the minutest details as to the preparation of reagents and manipulation of experiment prescribed for each determination. The most important "values" are the following :—

(1) Acid value.

(2) Saponification or Köttstorfer value.

(3) Reichert (Reichert-Meissl or Reichert-Wollny) value.

(4) Acetyl value.

(5) (Bromine or) Iodine value.

In addition to the above, the percentage of insoluble fatty acids

* *Berichte* **13**, 2277. † *J. S. C. I.* 1896, 15. ‡ *Berichte* **12**, 1768.

is sometimes referred to as the "Hehner value." It should be noted, however, that the insoluble fatty acids obtained from oils and fats after saponification contain varying amounts of unsaponifiable matter. Hence the term "Hehner value" comprises insoluble fatty acids + unsaponifiable matter. The "Polenske value" will be referred to in connection with the Reichert value.

The Acid Value.—This is determined by the number of milligrams of potassium hydrate (KOH) required to saturate the free fatty acids in one gram of oil, fat, or wax.

The standard alkali used in this process may be of $^N/_2$, $^N/_5$, or $^N/_{10}$ strength, according to the nature and amount of fat, and may be either in aqueous or alcoholic solution, and the indicator is preferably phenolphthalein. The sample may be dissolved in pure alcohol, methyl alcohol, purified methylated spirit, or a mixture of alcohol and ether; but whatever solvent is used it should be tested for acidity, and if any is present it is best neutralized exactly with $^N/_{10}$ alkali.

Liquid fats, say about 10 gm., are weighed into a flask, and about 50 c.c. of the neutral solvent, with a few drops of indicator, added. The titration is then made with constant shaking, the alkali solution being run in slowly.

The first appearance of a pink colour is accepted as the end; otherwise by standing a little time the colour may disappear, owing to saponification of neutral esters. Solid fats or waxes should be heated on a water-bath until the solvent boils, then at once titrated.

In some substances alcohol alone will not give a clear solution (which does not really matter), but if a clear solution is desired a mixture of ether and alcohol may be used and the titration made with alcoholic alkali. The number of c.c. of standard potash used taken in milligrams of KOH will give the calculation for acid value.

Lewkowitsch mentions that the free acid is sometimes calculated into percentage of oleic acid (mol. wt. 282·27), in which case the value will be obtained by multiplying the number of c.c. of $^N/_{10}$ alkali used by 0·0282, dividing by the weight of sample and multiplying by 100. In other cases, such as lubricating oils, the free fatty acids are sometimes calculated as SO_3, in which case the factor will of course be 0·004.

Köttstorfer on the other hand records the "degrees of acidity" by the number of c.c. of $^N/_1$ KOH required by 100 gm. of the fat.

EXAMPLE.—3·254 gm. of tallow treated as above required 3·5 c.c. of $^N/_{10}$ KOH or $3·5 \times 5·61$ mgm. KOH. Hence acid value $= \frac{3·5 \times 5·61}{3·254} = 6·03$.

Saponification or Köttstorfer value.—This indicates the number of milligrams of potassium hydroxide required for the complete saponification of one gram of a fat or wax. It expresses the amount of potassium hydroxide, in tenths per cent., required to neutralize the total fatty acids in 1 gram of a fat or wax.

The solutions required are :—

Standard hydrochloric acid.—Semi-normal strength, *i.e.*, 18·23 grams per litre.

Standard solution of caustic potash in alcohol.—This should contain about 30 gm. of KOH per litre. Methylated spirit,* previously digested with permanganate, a little dry calcium chloride afterwards added, then distilled, rejecting the first portions, may be used in place of pure alcohol. In any case the strength should not be less than 90 per cent., and the solution should be made from alcohol which will not give a yellow colour after being boiled with very strong solution of caustic potash and left standing for half an hour. As the solution changes in strength, it is not possible to rely upon its being semi-normal, but it should be roughly adjusted at about that strength with absolutely accurate hydrochloric acid, and a blank experiment made side by side with each titration of fat. It is best kept in the dark. The excess of potash used in the fat titration is thus expressed in terms of $^{N}/_{2}$ acid, and to arrive at the percentage of potash, each c.c. is multiplied by 0·02805. The "saponification equivalent" of the fat or oil is found by dividing the weight in milligrams of the sample by the number of c.c. of normal (not $^{N}/_{2}$) acid corresponding to the alkali neutralized by the oil. If the percentage of potash is known, the saponification equivalent may be found by dividing this percentage into 5611, or if NaHO is the alkali used, into 4001.

METHOD OF PROCEDURE: From 1·5 to 2 gm. of the fat, previously purified by melting and filtration, are carefully weighed into a Jena or other good glass flask fitted with a long cooling tube or an inverted condenser. 25 c.c. of standard alcoholic potash are then added, the mixture heated on the water-bath to gentle boiling, with occasional agitation, until a perfectly clear solution is obtained. Köttstorfer recommends heating for fifteen minutes; but in the case of butters this is generally more than sufficient; with other fats twenty minutes to half an hour may be required. At the end of the saponification the flasks are removed from the bath, a definite (not too small) quantity of phenolphthalein added, and the excess of potash titrated back with $^{N}/_{2}$ hydrochloric acid with as little exposure to the air as is possible.

EXAMPLE.—1·532 gm. of olive oil were saponified with 25 c.c. of alcoholic potash, and 12·0 c.c. of $^{N}/_{2}$ hydrochloric acid were required to titrate back. Another 25 c.c. of alcoholic potash measured out at the same time required for the blank test 22·5 c.c. of the standard acid.

Hence, the amount of potash used for saponification was

$$(22{\cdot}5 - 12{\cdot}0) \times 0{\cdot}02805 \text{ gm.} = 294{\cdot}5 \text{ mgm. KOH for } 1{\cdot}532 \text{ gm. fat.}$$

or for 1 gm. of fat

$$\frac{294{\cdot}5}{1{\cdot}532} = 192{\cdot}2 \text{ mgm. KOH.}$$

The method of calculation adopted by Köttstorfer is to ascertain the number of milligrams of KHO required to saturate the acids contained in 1 gm. of fat, or, in other words, parts per 1000. He found that, operating in this way, pure butters required from 221·5 to 232·4 mgm. of KHO for 1 gm., whereas the fats usually mixed

* "Industrial" methylated spirit is the most suitable for this purpose, as it remains clear on dilution with distilled water.

with butter, such as beef, mutton, and pork fat, required a maximum of 197 mgm. for 1 gm., and other oils and fats much less.

Practically this means that the amount of KHO required for genuine butters ranges from 23·24 to 22·15 per cent., the latter being the inferior limit. If caustic soda is used instead of potash, other numbers must of course be used.

The following list shows the parts of KHO required per 1000 of fat; the first four being calculated from their known equivalents, the rest obtained experimentally by Köttstorfer, Allen, Stoddart, or Archbutt:—

Tripalmitin	208·8	Linseed	192—195
Tristearin	189·1	Cotton Seed	193—195
Triolein	190·4	Whale	188—194
Tributyrin	557·3	Seal	189—196
Cocoanut Oil	246—260	Rape (Colza)	170—179
Dripping	197·0	Cod Liver Oil	171—189
Lard	195·4	Castor	183—186
Horse Fat	195—197	Sperm	123—147
Lard Oil	191—196	Shark Liver	161
Olive Oil	185—196		
Niger Oil	190·2		

A further application of this method may be made in determining separately the amounts of alkali required for saturating the free fatty acids and saponifying the neutral glycerides or other esters of any given sample of fat, oil, or wax (see Allen, *Organic Analysis* ii. 45, 76, also Lewkowitsch, 4th edit., vol. I., p. 301).

The Ester Value.—This indicates the number of milligrams of KOH required for the saponification of the neutral esters in one gram of a fat or wax.

Where the fat contains no free fatty acids the ester value is the same as the previously mentioned saponification value, but as many fats or waxes do contain small quantities of free fatty acids the saponification value includes both, and therefore the ester value is the difference between the saponification and the acid value.

The Reichert (Reichert-Meissl, Reichert-Wollny) value.—This indicates the number of cubic centimetres of $^{N}/_{10}$ KOH required for the neutralization of that portion of the soluble volatile fatty acids which is obtained from 2·5 (or 5) grams of a fat or wax by the Reichert distillation process.

Reichert originally used 2·5 gm. of substance, but Meissl suggested that 5 gm. would be a more convenient quantity, and this is the amount now generally used. Wollny, in his modification of the Reichert process, also uses 5 gm. of substance. It is important to note that this process and its modifications do not yield absolute values; they merely give a measure of the total volatile acids present in an oil, fat or wax. For purposes of comparison, especially in the examination of butter fat, the relative numbers thus obtained are of great value. The numbers given by the Meissl and Wollny modifications are not necessarily twice the

Reichert value. In the case of butter fat, however, it is quite admissible to work with 2·5 gm. and to multiply the result by 2·2 in order to obtain numbers comparable with those found by the Reichert-Meissl or the Reichert-Wollny process. On the other hand the quantity of 5 gm. must be rigorously adhered to in the case of cocoanut oil and palm kernel oil.

The description of the process as used for butter will practically apply to other fatty matters.

BUTTER.

The Reichert or Reichert-Meissl Method.—This process consists in saponifying the fat to be examined by an alkali, separating the fatty acids by neutralizing the alkali, and distilling off the volatile acids (chiefly butyric and caproic) for titration with standard acid. In this and Köttstorfer's method, where also alcoholic solution of caustic alkali is used, it is essential to avoid absorption of CO_2 by long exposure.

The necessary solutions are :—

1. Standard barium or potassium hydrate. $^{N}/_{10}$ strength is most convenient, but any solution approximating to that strength may be used, and a factor found to convert it to that strength in calculating the results of titration. It must be carefully preserved from CO_2 by any of the usual arrangements, and where a constant series of titrations are carried on, it is best to have a store bottle and burette fitted, as shown p. 12, fig. 11.
2. Phenolphthalein indicator, see p. 39.
3. Alcohol of about 90 per cent. strength, and free from acid or aldehyde.

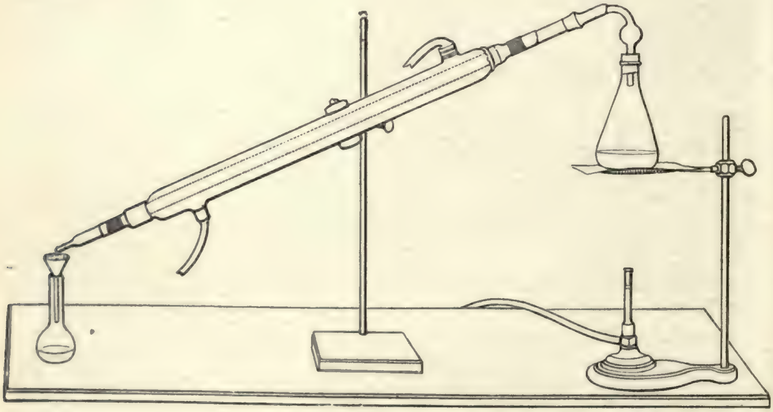


Fig. 56.

4. Solution of caustic soda. Made by dissolving 100 gm. of good sodium hydrate in 100 c.c. of distilled water which has been

recently well boiled and cooled; this solution will not be contaminated with CO_2 to any extent, since any Na_2CO_3 which might be formed is quite insoluble in the strong solution; it must be allowed to stand until quite clear, then poured off and well preserved. Or better than this, about 2 gm. of solid stick potash or soda may be added with 50 c.c. of 70 per cent. alcohol to 5 gm. of butter when commencing saponification.

5. Sulphuric acid for separating the fatty acids is made by diluting 25 c.c. of strongest H_2SO_4 to a litre with water.

6. The apparatus for digestion and distillation are shown in fig. 56, the same Erlenmeyer flask being used for the digestion and for the distillation. The distilled liquid drops into a small funnel containing a small porous filter for separating any scum which may pass over with the distillate; the receiver holding the funnel is marked at 50 c.c. and 100 c.c., so as to be available for either 2·5 gm. or 5 gm. of butter fat.

The following method of manipulation as drawn up by the Association of Official Agricultural Chemists, U.S.A., is recommended as being all that is required to ensure accuracy, and applies to the treatment of approximately 5 gm. of fat for each operation. Many operators prefer to take about half that quantity, which saves time, and need not be any the less accurate.

PROCESS: WEIGHING THE FAT: The butter or fat to be examined should be melted and kept in a dry, warm place at about 60° C. for two or three hours until the moisture and curd have entirely settled out. The clean supernatant fat is poured off and filtered through a dry filter-paper in a jacketed filter containing boiling water, to remove all foreign matter and any traces of moisture. Should the filtered fat in a fused state not be perfectly clear the treatment above mentioned must be repeated.

The saponification flasks are prepared by having them thoroughly washed with water, alcohol, and ether, wiped perfectly dry on the outside, and heated for one hour to 100° C. The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within fifteen or twenty minutes of the time they are weighed. The weight of each flask is determined accurately, using a flask for a counterbalance or not, as may be convenient. The weight of the flasks having been accurately determined they are charged with the melted fat in the following way:—

A pipette with a long stem marked to deliver 5·75 c.c. is warmed to a temperature of about 50° C. The fat having been poured back and forth once or twice into a dry beaker in order to thoroughly mix it, it is taken up in the pipette, the nozzle of the pipette carried to near the bottom of the flask, it having been previously wiped to remove any adhering fat. The 5·75 c.c. of fat are allowed to flow into the flask and the pipette is removed. After the flasks have been charged in this way they should be re-covered with the silk handkerchief and allowed to stand fifteen or twenty minutes, when they are again weighed to ascertain the exact amount of fat.

THE SAPONIFICATION: 10 c.c. of 90 per cent. alcohol are added to the fat in the flask, 2 c.c. of the concentrated soda solution or 2 gm. of solid alkali are added, a soft cork stopper inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flasks upon the water or steam bath. The flasks during the saponification, which should last for one hour, should be gently rotated from time to time, being careful not to project the soap for any distance up the sides of the flask. At the end of an hour the flasks, after having been cooled to near the room temperature, are opened. If solid alkali is used

instead of aqueous solution, alcohol of 75 or 80 per cent. in larger quantity may be used.

REMOVAL OF THE ALCOHOL: The stoppers having been laid loosely in the mouth of the flasks, the alcohol is removed by dipping the flasks into a steam bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and to avoid any loss from this cause, or any creeping of the soap up the sides of the flask, it should be taken from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapour may be removed from the flask by waving it briskly, mouth down, to and fro. Complete removal of the alcohol with the precautions above noted should take about forty-five minutes.

DISSOLVING THE SOAP: After the removal of the alcohol the soap should be dissolved by adding 100 c.c. of recently boiled distilled water, and warmed on the steam bath with occasional shaking until the soap is completely dissolved.

SETTING FREE THE FATTY ACIDS: When the soap solution has cooled to about 60° or 70° C., the fatty acids are separated by adding 40 c.c. of the dilute sulphuric acid mentioned above.

MELTING THE FATTY ACIDS: The flasks should now be re-stoppered as in the first instance, and the fatty acids melted by replacing the flasks on the steam bath. According to the nature of the fat examined the time required for the fusion of the fatty acids may vary from a few minutes to hours.

THE DISTILLATION: After the fatty acids are completely melted, which can be determined by their forming a transparent oily layer on the surface of the water, the flasks are cooled to room temperature and a few pieces of pumice stone added. The pumice stone is prepared by throwing it, at white heat, into distilled water, and keeping it under water until used. The flask is now connected with the condenser, slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 100 c.c. of the distillate in as nearly as possible thirty minutes.

Some operators distil 110 c.c. from 5 gm. of butter into an ordinary measuring flask, then filter and use 100 c.c. for titration, the number of c.c. of alkali used is multiplied by 1·1 which gives the Reichert-Meissl value.

The above methods of preparation are somewhat tedious, but experienced operators will find methods of working so as to occupy less time without loss of accuracy.

TITRATION OF THE VOLATILE ACIDS: The 100 c.c. of the filtered distillate are poured into a beaker holding from 200–250 c.c., 0·5 c.c. of phenolphthalein solution added, and decinormal barium or potassium hydrate run in until a red colour is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red colour produced remains apparently unchanged for two or three minutes.

Where the greatest accuracy is required it is best to carry out side by side a blank experiment with the same amounts of alcohol, alkali, etc.

It must be borne in mind that this method yields only a portion of the volatile fatty acids, but the experience of the author and a host of other very competent operators clearly shows that the distillate from 5 gm. of genuine normal butter fat produced in districts of medium temperature, when carried out as described, should require not less than 24 c.c. of $^{N}/_{10}$ alkali to neutralize the volatile acids present. It is true that butters known to be genuine have occasionally been found to give lower figures from some

unexplained causes, one of which seems to be due to milk taken from cows towards the end of their period of lactation. The figure may also rise to 32 or 33 c.c. of alkali. This is often the case with butters produced in warmer climates than Great Britain. The general average for butters taken from the mixed milk of a number of cows will be between 27 and 28 c.c., whereas margarine (except when consisting largely of cocoanut oil) will rarely require more than 0·5 c.c., beef fat and lard about the same, while cocoanut oil, which gives the highest figures, requires about 7 c.c.

It may, therefore, be concluded that any sample of butter fat which requires less than 24 c.c. of $^{N}/_{10}$ alkali must be looked upon with suspicion.

The minimum value recommended in Great Britain, France, and Germany, is 24 ; Sweden, 23 ; and Italy, 20.

A Joint Committee of the Principal of the Government Laboratory and the Society of Public Analysts, adopted in 1900* the Reichert-Wollny method as the official method for determining the percentage of butter-fat in margarine, the object in view being to avoid discrepancies which might arise through the employment of different methods by individual analysts. The following is the official description of the method :—

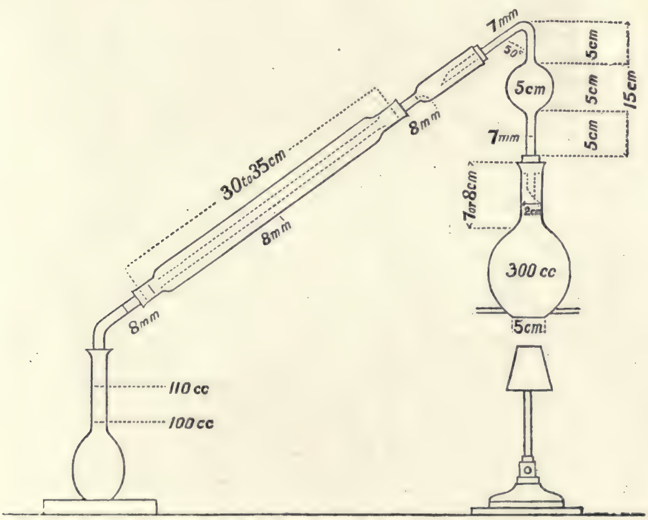


Fig. 57.

The Reichert-Wollny method for determination of volatile fatty acids in Margarine and Butter.—" Five gm. of the liquid fat are introduced into a 300 c.c. flask, of the form seen in the figure (length of neck 7 to 8 centimetres, width of neck 2 centimetres). Two c.c. of a solution of caustic soda (98 per cent.) in an equal

* See *Analyst,* 1900, 309.

weight of water—preserved from the action of atmospheric carbonic acid—and 10 c.c. of alcohol (about 92 per cent.) are added, and the mixture is heated under a reflux condenser, connected with the flask by a T-piece, for fifteen minutes in a bath containing boiling water. The alcohol is distilled off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water, which have been kept boiling for at least ten minutes, are added, and the flask heated until the soap is dissolved. Forty c.c. of normal sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube 7 millimetres wide and 15 centimetres from the top of the cork to the bend. At a distance of 5 centimetres above the cork is a bulb 5 centimetres in diameter. The flask is supported on a circular piece of asbestos 12 centimetres in diameter, having a hole in the centre 5 centimetres in diameter, and is first heated by a very small flame, to fuse the insoluble fatty acids, but the heat must not be sufficient to cause the liquid to boil. The heat is increased, and when fusion is complete 110 c.c. are distilled off into a graduated flask, the distillation lasting about thirty minutes (say from twenty-eight to thirty-two minutes), the distillate is shaken, 100 c.c. filtered off, transferred to a beaker, 0·5 c.c. of phenolphthalein solution (1 gm. in 100 c.c. alcohol) added, and the filtrate titrated with decinormal soda or baryta solution. Precisely the same procedure (with the same reagents), omitting the fat, should be followed, and the amount of decinormal alkali required to neutralize the distillate ascertained. This should not exceed 0·3 c.c. The volume of decinormal solution of alkali used, less the figure obtained by blank experiment, is multiplied by 1·1. The number so obtained is the "Reichert-Wollny Number."

NOTES ON THE METHOD: The sample is melted and filtered from curd and water through a dry filter. From the filtrate the 5 gm. of fat for the process are taken. The soda solution is filtered clear from carbonate formed in its preparation, and kept in a special bottle. The Soxhlet spherical condenser is a convenient one for the reflux distillation. This is fixed near the water-bath in which the saponification is to take place, and is connected with the flask by means of a T-piece and india-rubber tubes inclined at an angle of 45°. During the saponification the free limb of the T-piece is directed upwards, and its end closed by a short piece of india-rubber and glass rod. At the end of fifteen minutes this limb is turned downwards, and the piece of glass rod, replaced by a tube carrying away the alcohol.

One hundred c.c. of hot distilled water are added, and the flask frequently shaken until the soap is dissolved. The Liebig is a convenient form of condenser. One containing a column of water 30 to 35 centimetres in length gives sufficient condensing surface. After shaking the distillate, about 5 c.c. are filtered through a dry paper into a 100 c.c. flask. This serves to wash out the flask. When the 100 c.c. are transferred to a beaker, the flask is not washed out, but the main quantity is neutralized with the standard solution of alkali and returned to the flask, then again transferred to the beaker and the titration completed."

The somewhat lengthy process of saponification in the above method may advantageously be replaced by the following, due to Leffmann & Beam: *

* *Analyst*, 1891, **16**, 153; 1892, **17**, 65.

First, prepare a solution of 100 gm. caustic soda (98-99 % powdered caustic answers well) in water and make up to 200 c.c. Put the solution in a bottle with a rubber stopper and allow to stand till quite clear. 25 c.c. of the clear solution are then pipetted into 125 c.c. of pure glycerin in a flask and well mixed. Next 5 gm. of the fat are placed in a 300 c.c. flask, 10 c.c. of the glycerol-soda added and the flask heated cautiously over a small Bunsen flame. Much foaming takes place, and the flask should be vigorously shaken. Complete saponification takes place in less than five minutes, the process being complete when the foaming has entirely ceased. The hot soap is then dissolved at once in 90 c.c. of water that has recently boiled, adding it drop by drop at first. Then 40 c.c. of dilute sulphuric acid are added, together with a few pieces of pipe-clay, and the distillation proceeded with as above. The usual blanks are 0·2 – 0·3 c.c. of $^{N}/_{10}$ alkali for the 110 c.c. of distillate.

The glycerol-soda solution should be kept in a flask closed with a rubber stopper and measured by means of a rather wide glass tube marked to deliver 10 c.c.

Lewkowitsch* testifies to the fact that the values obtained by the above method are practically identical with that obtained by the Reichert-Wollny process.

The water-insoluble Volatile Fatty Acids. (Polenske.)

This determination is best made by Polenske's method which is carried out as follows :—

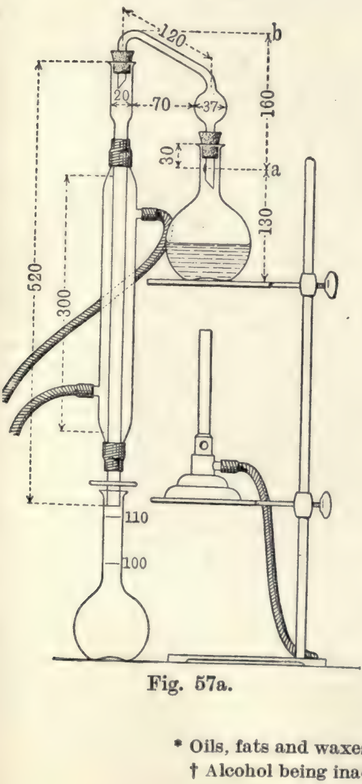


Fig. 57a.

Saponify 5 gm. of the filtered butter-fat by the Leffmann-Beam† process described above, taking care not to overheat the mixture of fat and glycerol-soda. Allow to cool below 100° C. before adding 90 c.c. of water, and dissolve the mass by warming on the water-bath to about 50° C. The solution must be clear and almost colourless; if of a brown colour, the test must be rejected. To the hot soap solution add 40 c.c. of the dilute sulphuric acid and 0·1 gm. of *finely powdered* pumice and attach immediately to the condenser. The apparatus used must agree in all details with the dimensions given in fig. 57a. Regulate the heat so that in 19-20 minutes 110 c.c. are distilled over, and the flow of water through the condenser so that the distillate does not drop into the 110 c.c. flask at a higher temperature than 20-23° C. When 110 c.c. have distilled over, remove the burner and replace the flask

* Oils, fats and waxes, 4th edition, Vol. I., 334.

† Alcohol being inadmissible in this process.

by a 20 c.c. measuring cylinder. The 110 c.c. flask which must not be shaken, is immersed almost completely in water at 15° C. After five minutes' standing the neck is gently tapped so that the oily drops floating on the surface may adhere to the walls of the flask. After a further ten minutes the consistence of the insoluble acids is noted, with a view to ascertaining whether they form a semi-solid mass or oily drops. The flask is then corked and its contents mixed by turning it upside down several times, avoiding, however, any violent shaking. 100 c.c. are then filtered through an 8 cm. dry filter and titrated with $^N/_{10}$ barium or potassium hydroxide, as in the Reichert-Wollny process. The insoluble volatile acids on the filter are washed three times in succession with 15 c.c. of water that has previously been passed successively through the tube of the condenser the 20 c.c. measuring cylinder, and the 110 c.c. flask. These wash waters are rejected. The water-insoluble volatile acids are then collected by rinsing the condenser, cylinder and flask three times in succession with 15 c.c. of neutralized 90 per cent. alcohol, and the alcoholic washings poured on to the filter —each being allowed to pass completely through before the next washing is added. The alcoholic filtrate is then titrated with $^N/_{10}$ alkali. The figure so obtained is called the Polenske value. For butter it varies from 1·5 to 3·0 c.c. and for cocoanut oil from 16·8-17·8 c.c. In order to obtain concordant results with this method, it is absolutely essential to follow the procedure given above in all its minutest details.

Lewkowitsch found that the Polenske values of genuine French and Finnish butters ranged from 2·24—4·1, and those of cocoanut oil from 15·5—20·45, while palm kernel oil gives values lying between 10 and 12. Several attempts have been made to determine the proportions of cocoanut oil in mixtures of cocoanut oil and butter fat by means of the Polenske number, but in view of the above range of values quantitative results should be received with great caution, especially with regard to alleged small additions of cocoanut oil to butter fat. Tatlock and Thomson* have also critically examined this process and express the opinion that "the possibility of the detection of even 10 per cent. of cocoanut oil in a butter by the Polenske method is very doubtful." But in the case of margarine "the Polesnke number appears to be quite reliable within limits of say 5 per cent." They obtained results within 3 per cent. of the truth, where there was 35 per cent. of cocoanut oil present. Margarine containing no cocoanut oil gave 0·4 Reichert-Wollny and 0·5 Polenske values.

The Acetyl Value.—This indicates the number of milligrams of KOH required for the neutralization of the acetic acid obtained on saponifying 1 gm. of an acetylated oil, fat, or wax. This treatment of fats was introduced by Benedikt, and a process by himself and Ulzer for acetylation and determination was arranged; but as the results were not consistent with modern ideas, Lewkowitsch† modified the method and proposed to determine the true acetyl value by actually titrating the amount of acetic acid assimilated by the hydroxylated acid in the form of acetyl C_2H_3O and given up on saponification as acetic acid to the standard alkali.

* *J. S. C. I.* 1909, 69. † *J. S. C. I.* 1897, 503.

The method is as follows :—

METHOD OF PROCEDURE : 10 gm., or any other convenient quantity, are boiled with twice the amount of acetic anhydride for two hours in a round-bottomed flask attached to an inverted condenser. The solution is then transferred to a beaker of about 1 litre capacity, mixed with 500—600 c.c. of boiling water and heated for half an hour, whilst a slow current of carbon dioxide is passed into the liquid through a finely drawn out tube reaching nearly to the bottom of the beaker ; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is siphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed —this being ascertained by testing with litmus paper. Prolonged washing beyond the required limit causes slight dissociation of the acetyl product. This would lead to too low an acetyl value. The acetylated product is then filtered through a dry filter-paper in a drying oven to remove water.

This operation may be carried out quantitatively, and in that case the washing is best done with boiling water on a weighed filter. On weighing the acetylated oil or fat, an increase of weight would prove that assimilation of acetyl groups had taken place. This method may be found useful to ascertain preliminarily whether a notable amount of hydroxylated acids is present in the sample under examination.

About 5 gm. of the acetylated product are then saponified by means of alcoholic potash solution as in the well-known determination of the saponification value. If the "*distillation process*" be adopted it is not necessary to work with an accurately measured quantity of standardized alcoholic potash. In case the "*filtration process*" be used, the alcoholic potash must be measured exactly. (It is, however, advisable to employ in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat). Next, the alcohol is evaporated and the soap dissolved in water. From this stage the determination is carried out either by (*a*) the "distillation process" or (*b*) the "filtration process."

(*a*) DISTILLATION PROCESS.—Add dilute sulphuric acid (1 : 10) more than is required to saturate the potash used, and distil the liquid as is usual in Reichert's distillation process. Since a large quantity of water must be distilled off, either a current of steam is blown through the suspended fatty acids or water is run into the distilling flask, from time to time, through a stoppered funnel fixed in the cork, or any other convenient device is adopted. It will be found quite sufficient to distil over 500 to 700 c.c., as the last 100 c.c. contain practically no acid. Then filter the distillates to remove any insoluble acids carried over by the steam, and titrate the filtrate with $^{N}/_{10}$ potash, phenolphthalein being the indicator. Multiply the number of c.c. by 5·61, and divide the product by the weight of substance taken. This gives the *acetyl value.*

(*b*) FILTRATION PROCESS. — Add to the soap solution a quantity of standardized sulphuric acid *exactly* corresponding to the amount of alcoholic potash employed, and warm gently, when the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated fatty acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with $^{N}/_{10}$ potash, using phenolphthalein as indicator. The acetyl value is calculated in the manner shown above.

Both methods give identical results, but (*b*) will be found shorter and more convenient than (*a*).

The distilled water used in determining the value by either the distillation or the filtration process should be carefully freed from CO_2 by previous boiling, as otherwise serious errors may be made. Even the water used for generating steam in the distillation process should be brought to violent ebullition before the steam is passed into the distilling flask. This source of error many easily occur in the case of very hard water. Check experiments with pure acetic acid will readily guide the operator, if necessary. In order to facilitate the separation

of the insoluble fatty acids in the filtration process, it will be found useful to add a slight excess of mineral acid. Of course this amount must be measured accurately, and deducted from the alkali required for determining the dissolved acids.

A full discussion as to the meaning of the acetyl value in fat analysis will be found in a lengthy paper by Lewkowitsch in *The Analyst*, 1899, 319.

The Bromine Value.—This indicates the percentage of bromine absorbed by a fat or wax. This determination was proposed by Cailletet in 1857; but the method of carrying it out is due to Mills* and his collaborators Snodgrass and Akitt. Mills found that it was of the utmost importance rigidly to exclude moisture when making the determination, since in the presence of water the value obtained was too high. He dissolved the sample of dried and filtered fat in carbon tetrachloride, added a standard solution of bromine in carbon tetrachloride in excess, and titrated back the excess with a standard solution of β-naphthol in carbon tetrachloride, when monobromonaphthol is formed. As, however, this determination has now been entirely superseded by the determination of Iodine value, the reader is referred, for further information, to the original papers on the subject already mentioned.†

The Iodine Value.—This indicates the percentage of iodine chloride, expressed in terms of iodine, absorbed by a fat or wax. "This value is a measure of the proportion of unsaturated fatty acids, which, both in their free state and in combination with glycerol, have the property of assimilating halogens with formation of additive compounds."—(Lewkowitsch.) The method by which the determination was carried out was originated by Hübl,‡ who proved that from an alcoholic solution of iodine, in the presence of mercuric chloride, glycerides of the unsaturated fatty acids absorb iodine in a very regular, well-defined manner, when kept at the ordinary temperature, so that quantitative results can be obtained.

The following solutions are required for Hübl's process :—

1. Standard iodine solution.—This is made by dissolving respectively 5 gm. of iodine and 6 gm. of mercuric chloride, each as pure as possible, in separate portions of 100 c.c. each of 95 % alcohol, then mixing the two liquids, and allowing to stand for 12 to 24 hours before use. This solution must always be standardized at the time of using, and it is advisable not to mix a large quantity unless it is required for immediate use.

2. Solution of Sodium Thiosulphate.—Prepared by dissolving about 24 grams of the crystallized salt in a litre of water. It is standardized either by dissolving about 0·25 gram of re-sublimed iodine, most accurately weighed, in potassium iodide solution and

* *J. S. C. I.* 1883, 435; 1884, 366.

† A process for determining "the bromine addition" and "the bromine substitution" has been recorded by McIlhiney, *J. S. C. I.*, 1894, 668 also *J. Am. C. S.*, 1899, 1084, and 1902, 1109.

‡ *Dingler's Polyt. Journal* 1884, 281.

running in the thiosulphate solution from a burette till the solution has only a light yellow colour, then adding starch solution and continuing the addition of thiosulphate till the blue colour just disappears; or by the following method,* due to Volhard:—Dissolve exactly 3·8657 gm. of pure potassium dichromate in a litre of water. Place in a stoppered bottle 10 c.c. of a 10 per cent. solution of potassium iodide and 5 c.c. of hydrochloric acid, and run in from a burette exactly 20 c.c. of the dichromate solution. In this way 0·2 gm. precisely of iodine will be set free, which is then titrated as described above. The dichromate solution maintains its strength indefinitely, hence is always ready for standardizing a thiosulphate solution.

3. Chloroform or Carbon Tetrachloride.—These should stand the following test for purity. Mix 10 c.c. with 10 c.c. of the iodine solution, allow to stand for 2 or 3 hours, and titrate. The volume of thiosulphate required should be the same as that required for 10 c.c. of the iodine solution alone.

4. Potassium iodide Solution.—A 10 per cent. solution of the pure salt is used.

5. Starch solution.—This should always be freshly made. About 0·5 gm. of starch is shaken with a little cold water in a test-tube, poured into about 50 c.c. of hot water in a larger tube, the liquid raised to the boiling point, then cooled for use.

METHOD OF PROCEDURE: From 0·15 to 0·2 gm. of a drying or fish oil; 0·2 to 0·3 gm. of a semi-drying oil; 0·3 to 0·4 gm. of a non-drying oil; or 0·8 to 1 gm. of a solid fat is dissolved in 10 c.c. of chloroform or carbon tetrachloride in a well-stoppered, wide-mouthed bottle of about 300-400 c.c. capacity, and 25 c.c. of the iodine solution run in from a pipette, which should be drained for exactly 15 seconds. After not less than four hours' standing in a dark place the liquid should possess a dark brown tint; in any circumstances it is necessary to have a considerable excess of iodine (at least double the amount absorbed ought to be present) and the period of standing should be from four to six hours. At the end of that time some strong solution of potassium iodide should be added and about 150 c.c. of water (more iodide being added if the liquid does not remain clear), and standard thiosulphate run in at once from a burette, with constant shaking, till the liquid becomes yellow. Starch solution is then added and the titration finished in the usual way.

If after standing, say two hours, the solution has lost its deep colour brown, it is best to make a fresh experiment with either less fat or more iodine solution.

A blank experiment should in every case be made side by side with the sample, using the same proportions of chloroform and iodine solution.

EXAMPLE.—To 0·4120 gm. of olive oil 10 c.c. of chloroform and 25 c.c. of Hübl's solution were added and allowed to stand for four hours. At the end of that time 18·9 c.c. of thiosulphate were required. The blank, consisting of 10 c.c. of chloroform and 25 c.c. of Hübl's solution, required 46·9 c.c. thiosulphate. Also

(i.) 0·2704 gm. Iodine required 21·3 c.c. thiosulphate.
(ii.) 0·2076 ,, ,, ,, 16·35 c.c. ,,

$$\frac{\cdot 2704}{21 \cdot 3} = \cdot 012695 \qquad \frac{\cdot 2076}{16 \cdot 35} = \cdot 0127$$

Hence 1 c.c. thiosulphate = ·0127 gm. Iodine.

* Lewkowitsch, Oils, Fats and Waxes, 4th Edition, Vol. I. p. 312.

$$\text{Iodine value} = \frac{(46 \cdot 9 - 18 \cdot 9) \times \cdot 0127 \times 100}{0 \cdot 412}$$
$$= \frac{28 \times 1 \cdot 27}{0 \cdot 412}$$
$$= 86 \cdot 3$$

The values obtained by Hübl for various oils and fats are given in J. S. C. I., 1884, 642.

The relative proportions in which two oils are mixed can be deduced from the iodine value of the mixture, thus

Let Ia be the mean iodine value of an oil a.
Ib ,, ,, ,, b.
I the iodine value of the mixture.

Then

$$\text{percentage of oil a} = \frac{100\ (\mathrm{I} - \mathrm{Ib})}{\mathrm{Ia} - \mathrm{Ib}}$$

EXAMPLE.—A mixture of cotton seed and olive oils gave the iodine value 91, hence

$$\text{cotton seed oil} = \frac{100\ (91 - 85)}{109 - 85} = 25 \text{ per cent.}$$

The valuable improvement made by Wijs* produces an iodine solution which holds its standard strength for a very much longer period than the original Hübl solution, and also acts much more rapidly. The same results are eventually obtained as in the original Hübl process when the latter is carefully performed.

The method proposed by Wijs is the use of a solution of iodine monochloride in strong acetic acid, in place of the mixture of iodine and mercuric chloride. The original acid used was of 95 per cent. strength, but a much better solution is obtained by using acid of not less than 99 per cent.

Wijs admits a decrease of about 0·3 per cent. in 96 hours when using very pure 95 per cent. acid, but Lewkowitsch found it amounted to 4 per cent. in 64 hours. This Wijs attributed to the use of a less pure acid than was used by himself. However, the substitution of the stronger acid seems to settle the difficulty completely. Lewkowitsch states that he has found with 99 per cent. acid the same strength remains for two months ; other operators have not found it quite so permanent as this, but all agree that it does not alter so as to cause inconvenience. So far as the weakening of the acetic acid iodine solution is concerned, A. Marshall† is of opinion that it must largely depend upon the amount of chloracetic acid formed in preparing the solution. Wijs himself is of opinion that if the acid is pure, and especially free from oxidizable matters, there should theoretically be no possibility of any diminution of strength.

The preparation of Wijs' iodine solution is carried out as follows : 13 gm. of pure iodine are dissolved in a litre of 99 per cent. acetic acid ; the strength is then determined by standard thiosulphate, then chlorine gas, washed and dried, is passed into it until the titer is doubled. With a little practice the proper ending of the chlorination is ascertained by the change of colour from dark brown

* *Berichte*, 1898, 750. † *J. S. C. I.*, 1900, 213

to light yellow. If the gas is passed in until this just occurs the first titration may be dispensed with. The process of titrating the fat is carried out precisely as above described, with the exception that the time required for the absorption is very greatly curtailed. When small quantities of fat are used which are of low iodine value the action is complete in less than five minutes, and with values below 100 half an hour is quite sufficient. Lewkowitsch* strongly recommends Wijs' process. He finds it preferable to the Hübl iodine solution in almost every case, as it is infinitely superior to the latter as regards stability. He has known a solution to keep its strength practically unchanged for five months. It can be prepared rapidly, and the time spent on the test is very much shortened.

PHENOLS AND CRESOLS.

Phenol $C_6H_5OH = 94{\cdot}05$.

Cresol $C_6H_4 (CH_3) OH = 108{\cdot}06$.

THE chief method claiming accuracy for the determination of phenols volumetrically was originated by Koppeschaar†, and consists in precipitating the phenol from its aqueous or dilute alcoholic solution with bromine water in the form of tribromphenol. The strength of the bromine water was established by Koppeschaar by titration with thiosulphate and potassium iodide with starch.

Allen modifies the method as follows:—

METHOD OF PROCEDURE: a certain weight of the sample is dissolved in water, as much as corresponds to 0·1 gm. of phenol is taken out and put into a stoppered bottle holding 250 c.c. Further, to 7 c.c. of normal soda solution (=0·04 gm. NaOH per c.c.) bromine is gradually added till a yellow colour appears and remains; the liquid is then boiled till it has become colourless again. It now contains 5 molecules of sodium bromide and 1 of sodium bromate. When completely cooled, it is put into the phenol solution, after which 5 c.c. concentrated hydrochloric acid are at once added, and the bottle stoppered and shaken for some time. The reactions are:—

$$\text{I.}\quad 5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3Br_2 + 3H_2O.$$
$$\text{II.}\quad C_6H_6O + 6Br = C_6H_3Br_3O + 3HBr.$$

The bromine set free in the first, and not fixed by phenol in the second reaction must be still free, and is determined by adding potassium iodide and titrating the iodine liberated by $^N/_{10}$ thiosulphate:—

$$\text{III.}\quad 2KI + Br_2 = 2KBr + I_2.$$
$$\text{IV.}\quad I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$

For this purpose the bottle is allowed to stand for 15 or 20 minutes; a solution of about 1·25 gm. potassium iodide (free from iodate) is added, the bottle is stoppered, shaken up, and allowed to rest. Its contents are now poured into a beaker; the bottle is rinsed out, a little starch solution is added, and thiosulphate is run in from a burette till the blue colour is gone. (It will be best not to add the starch till the colour of the liquid has diminished to light yellow.)

* Oils, fats and waxes, 4th Edition, Vol. I. 323.

† *Z. a. C.* **16**, 233.

Where a number of determinations have to be made a standard solution of sodium bromide and bromate should be made by measuring out 100 c.c. of N. NaOH into a beaker, adding bromine till the liquid becomes brown in colour and smells distinctly of bromine, then heating the solution till quite colourless. It is then cooled and diluted to 1 litre.

1 c.c. = 0·007992 gm. bromine
= 0·001568 gm. phenol.
= 0·001801 gm. cresol.

Also 1 Br. corresponds to 0·19613 phenol.
1 ,, ,, ,, 0·22537 cresol.
Hence 79·92 Br. = 15·68 Phenol.
= 18·01 Cresol.

$$\text{and Iodine} \times \left(\frac{15{\cdot}68}{126{\cdot}92} = \right) {\cdot}1235 = \text{phenol.}$$

$$\text{,,} \quad \times \left(\frac{18{\cdot}01}{126{\cdot}92} = \right) {\cdot}1419 = \text{cresol.}$$

EXAMPLE.—5 gm. carbolic powder are put into a 250 c.c. flask, HCl added, and made up to the mark with water. The flask is shaken and the contents filtered. 50 c.c. of the filtrate (= 1 gm. of sample) are measured into a bottle and 100 c.c. of the bromide and bromate solution added, together with a little more HCl, and allowed to stand for 15 minutes. KI solution is then added and the Iodine set free titrated with $^N/_{10}$ thiosulphate. Suppose that 13·8 c.c. of the latter are required, and that titration with Iodine showed that 1 c.c. of it = 0·0121 gm. iodine; also that 10 c.c. of the bromide and bromate solution and KI required 10·5 c.c. thiosulphate. Then 100 c.c. of the bromide and bromate solution = 105 c.c. $^N/_{10}$ thiosulphate of which 105 − 13·8 = 81·2 c.c. represent the bromine absorbed, which has been determined in terms of Iodine.

Hence 81·2 × ·0121 × ·1235 = ·1214 gm. phenol or 12·14 per cent.

For the determination of phenol in raw products, Töth* modifies the bromine method as follows:—

METHOD OF PROCEDURE: 20 c.c. of the impure carbolic acid are placed in a beaker with 20 c.c. of caustic potash solution of 1·3 sp. gr., well shaken and allowed to stand for half an hour, then diluted to about ½ litre with water. By this treatment the tarry constituents are set free, and may mostly be removed by filtration; the filter is washed with warm water, until all alkali is removed. The filtrate and washings are acidulated slightly with HCl, and diluted to 3 litres. 50 c.c. are then mixed with 150 c.c. of standard bromide solution and then 5 c.c. of concentrated HCl. After twenty minutes, with frequent shaking, 10 c.c. of iodide solution are added, mixed, and allowed to rest three to five minutes, then starch, and the free iodine titrated with a sodium thiosulphate solution containing 9·779 grams of the crystals per litre (exactly corresponding to 5 grams iodine†.)

EXAMPLE.—20 c.c. raw carbolic oil were treated as above described. 50 c.c. of the solution, with 150 c.c. bromide solution (made by dissolving 2·04 gm. sodium bromate and 6·959 gm. sodium bromide to the litre), then 5 c.c. of HCl, required 17·8 c.c. of thiosulphate for titration. The 150 c.c. bromide = 0·237 gm. Br. The 17·8 c.c. thiosulphate required for residual titration = 0·052 gm. Br. leaving 0·185 gm. Br. for combination with the phenol.

* *Z. a. C.* **25**, 160, also *Analyst*, 1886, **11**, 92.

† Of course this solution would not maintain its strength on keeping, and it is extremely doubtful whether the solution could be depended on even when freshly made to have exactly the iodine equivalent given. It is best to standardize it against pure iodine (see Iodine Value of Oils).

As 50 c.c. have been taken out of a total volume of 3000 c.c. (representing 20 c.c. of the sample), we have $0 \cdot 185 \times 0 \cdot 19613 \times 60 = 2 \cdot 177$ gm. phenol or $2 \cdot 177 \times 5 = 10 \cdot 89$ per cent.

Kleinert* suggests, and his experiments appear to prove, that in titrating acid creosote oil by Koppeschaar's method for phenol, a serious error occurs in virtue of such oil containing substances of higher boiling-point than phenol, which are soluble in water, and behave with bromine in the same manner as true phenol.

Messinger and Vortmann† describe a method of determining phenol based on the fact that iodine combines with phenol in alkaline solution in the proportion of 6 atoms I to 1 mol. phenol.

METHOD OF PROCEDURE : 2 to 3 gm. phenol are dissolved in caustic soda solution (3 eq. NaHO to 1 eq. phenol) and made up to 500 c.c. with water ; 10 c.c. of this are placed in a flask, warmed to 60° C., and $^{N}/_{10}$ iodine added until the solution is faintly yellow, with formation of a red precipitate. When cold, the solution is acidified with dilute H_2SO_4, made up to 500 c.c. and filtered. In 100 c.c. of the filtrate, the excess of I is titrated with $^{N}/_{10}$ thiosulphate ; this amount, deducted from the total I used, gives the amount absorbed by phenol, which, when multiplied by 0·1235, gives amount of phenol in the sample.

A method for the examination of commercial phenols has been described by S. B. Schryver‡, and is based on the interaction of sodamide and bodies containing a hydroxyl group, which takes place according to the typical reaction :

$$NaNH_2 + C_6H_5OH = C_6H_5ONa + NH_3.$$

METHOD OF PROCEDURE : A 200 c.c. wide-necked flask is fitted with a separating funnel, the tube of which passes to the bottom, and an inverted condenser connected at its upper end with an absorbing vessel, and thence with an aspirator. About 1 gm. of sodamide is finely ground, washed two or three times with benzene by decantation, then introduced into the flask, and 50 or 60 c.c. of benzene (free from thiophen) added. The mixture is heated on a water-bath in a current of dry air freed from CO_2 for some ten minutes till the last traces of ammonia are expelled. About 20 c.c. of normal sulphuric acid are next placed in the receiver, and the phenol dissolved in six times its weight of benzene, is brought into the funnel and allowed to drop into the flask. The funnel is rinsed with more benzene, and the current of air is maintained through the boiling liquid for 75 minutes. The excess of sulphuric acid is finally titrated with normal sodium carbonate and methyl orange. With phenol, cresol, and guaiacol (alone), the process gives correct results, provided (1) the apparatus and phenol are perfectly dry (sodamide acts upon water), (2) sufficient benzene is employed to hold the sodium salt in solution, (3) the benzene is free from thiophen, and (4) air is aspirated for a sufficient length of time. Toluene or xylene may replace the benzene, but in that case a sand-bath must be used instead of the water-bath.

The process is obviously not applicable to the determination of the relative proportions of more than two phenols ; but it has been tested on mixtures of phenol and cresol, on wood-tar guaiacol, which is a mixture of guaiacol and creosol, on thymol in oil of thyme, and on eugenol in oil of cloves. Calling the number of c.c. of standard acid that are necessary to neutralize the ammonia given off when 1 gm. of a phenol (either simple substance or mixture) is treated with an excess of sodamide under the experimental conditions

* *Z. a. C.* **33**, 1. † *Ber.* 1890, 2753, and *J. S. C. I.* 1890, 1070.
‡ *J. S. C. I.* 1899, 553.

the "hydroxyl value"—which in the case of pure phenol is $\left(\frac{100}{9{\cdot}4}=\right)$ 10·63, and in that of pure cresol is $\left(\frac{100}{10{\cdot}8}=\right)$ 9·26, etc.—a table may be prepared for converting the hydroxyl value obtained when a mixture of two known phenols is operated upon directly into the relative proportion between the two ingredients, and the results calculated in this manner from the analysis of materials of the above-mentioned composition appear to be fairly satisfactory.

The method is equally available for determining the amount of water in any particular phenol, because the reaction between sodamide and water is analogous to that between the amide and a phenol. Fused sodium acetate is the best substance to remove the last traces of moisture from ordinary phenol, and the determination of moisture can be made by two experiments, one before and one after drying—the difference in ammonia represents the moisture. The process has an advantage over methods involving the use of bromine or iodine, as the results are not affected by the presence of hydrocarbons, for which reason it should be useful for determining phenols in a large number of essential oils, etc. Sodamide acts upon ketones, amines, etc.*, but these bodies can be readily removed by various suitable reagents.

SALICYLIC ACID.

$$C_6H_4\,(OH)\,COOH = 138{\cdot}05.$$

SEVERAL methods have been proposed for the determination of this substance as existing in the form of salts or in a free state, and a critical examination of the most hopeful of these has been carefully made by W. Fresenius and L. Grünhut†. The experiments were made on pure sodium salicylate. The method proposed by Messinger and Vortmann in which it is said by the authors that 1 mol. of salicylic acid consumes 6 atoms of iodine was not confirmed in these experiments, and they came to the conclusion that the method could not be relied on to give even approximately correct results. On the other hand their experience of Freyer's bromine method was that it gave satisfactory results.

The method described by Freyer‡ is based on the facts that, on mixing a solution of salicylic acid with bromine water in excess, a yellowish-white precipitate is formed.

$$C_6H_4{<}^{OH}_{COOH} + 4Br_2 = C_6HBr_3OBr + 4HBr + CO_2\,;$$

and that, on adding a solution of potassium iodide, not only does the excess of bromine liberate an equivalent amount of iodine, but the tribromphenol bromide also reacts as in the equation:

$$C_6H_2Br_3.OBr + 2KI = C_6H_2Br_3.OK + KBr + I_2.$$

* Titherley, *J. C. S. Trans.* 1897, 460.

† *Z. a. C.* 1899, 292, also *Analyst*, 1900, 19.

‡ *Chem. Zeits.* 20, 820.

Hence, in calculating the results, only 6 atoms of bromine correspond to one molecule of salicylic acid.

Freyer states that an excess of about 100 per cent. of bromine is necessary, but the authors have proved that an excess of from 75 to 80 per cent. is sufficient. They have tested the method with concentrated bromine solutions, using considerable quantities of sodium salicylate, and have obtained as satisfactory results as Freyer himself. They give the following details of their method of working, in which, like Freyer and Koppeschaar, they used solutions of potassium bromate and bromide, and liberated the bromine by the addition of hydrochloric acid.

METHOD OF PROCEDURE: The required quantity of the bromide and bromate solution is diluted with 300 c.c. of water, and decomposed with 30 c.c. of dilute HCl (sp. gr. 1·10). Into this mixture is introduced with continual stirring a solution of about 1 per cent. in strength of the substance under examination. A white precipitate is immediately formed, and, after this has been allowed to stand for about five minutes with occasional agitation, 30 to 40 c.c. of a 10 per cent. solution of KI are introduced and the separated iodine titrated with $^N/_{10}$ thiosulphate.

In the most successful results the bromide solution contained 2·5 gm. of potassium bromate, and about 10 gm. of potassium bromide in a litre of water. 25 c.c. of this solution corresponded with 25·5 c.c. of thiosulphate solution, and 1 c.c. of the latter to 0·01098 gm. of iodine or 0·00199 gm. of salicylic acid.

The percentage of salicylic acid thus found in the same sample of pure sodium salicylate varied in four determinations from 86·21 to 86·43 per cent. The theoretical amount is 86·23 per cent.

This method is not applicable to the analysis of mixtures of starch and sodium salicylate such as occur in medicinal tabloids. In such cases the substance should be dissolved in 90 per cent. alcohol, the solution brought to a definite volume, filtered from the undissolved starch, and an aliquot part of the filtrate used for the analysis. In a mixture of 90·91 per cent. of sodium salicylate and 9·09 per cent. of starch, the authors found in this way 89·97 per cent. of the former.

In the analysis of wines which contain sulphurous acid, aldehyde, and other substances which act upon bromine, the best method of determining salicylic acid, when present, is to make the liquid alkaline, concentrate it, render it acid, and extract it with a mixture of ether and petroleum spirit. The extract thus obtained is shaken with alkaline water, which removes the salicylic acid, and this aqueous solution can then be used in the bromine method.

As regards the colorimetric method of determining salicylic acid by means of ferric chloride, the author states that it can only be used when the amount of salicylic acid is less than 2 mgm.*

The Departmental Committee in their Report on Preservatives and Colouring Matters in Food (1901) recommend that salicylic acid be not used in a greater proportion than 1 grain per pint in liquid food and 1 grain per pound in solid food and that its presence in all cases be declared.

Methyl salicylate. $C_6H_4(OH).COO(CH_3)$.—E. Kremers and M. M.

* For the colorimetric determination of salicylic acid in Foodstuffs, see *Analyst*, 1905, 124.

James* have slightly modified the method proposed by Ewing, and boil a weighed quantity of the substance with a known volume of normal alkali for 5 minutes. The excess of alkali is then titrated with normal acid, and the alkali consumed, multiplied by 0·152, represents the weight in grams of methyl salicylate.

The method proposed by Messinger and Vortmann is also recommended. 5 gm. of the sample are saponified with excess of alkali, and when cold diluted to 500 c.c.; 10 c.c. of this are heated, 50 c.c. of $^{N}/_{10}$ iodine solution added, and the liquid diluted to 500 c.c.; in 100 c.c. of this, the excess of iodine is determined by means of $^{N}/_{10}$ sodium thiosulphate. 1 c.c. of iodine solution absorbed, when multiplied by 0·002535, represents the amount of methylic salicylate, as 1 mol. of the ethereal salt absorbs 6 atoms of iodine.

* *Chem. Centr.* 1898, 1070.

PART VI.

SPECIAL APPLICATIONS OF THE VOLUMETRIC SYSTEM TO THE ANALYSIS OF URINE, POTABLE WATERS, SEWAGE, ETC.

ANALYSIS OF URINE.

THE complete and accurate determination of the normal and abnormal constituents of urine presents more than ordinary difficulty to even experienced chemists, and is a hopeless task in the hands of any other than such. Fortunately, however, the most important matters, such as urea, glucose, phosphates, sulphates, and chlorides, can all be determined volumetrically with accuracy by ordinary operators, or by medical men who cannot devote much time to practical chemistry. The researches of Liebig, Neubauer, Bence Jones, Vogel, Beale, Hassall, Pavy, Allen, and others, have resulted in a truer knowledge of this important secretion; and to the two first mentioned chemists we are mainly indebted for the simplest and most accurate method of determining its constituents. With the relation which the proportion of these constituents bears to health or disease, the present treatise has nothing to do, its aim being simply to point out the readiest and most useful methods of determining them quantitatively.

The gram system of weights and measures will be adopted throughout this section, while those who desire to use the grain system will have no difficulty in working, when once the simple relation between them is understood* (see p. 27). The question of weights and measures is, however, of very little consequence, if the analyst considers that he is dealing with relative parts or proportions only; and as urine is generally described as containing so many parts of urea, chlorides, or phosphates, per 1000, the absolute weight may be left out of the question. The grain system is more readily calculated into English ounces and pints, and therefore is generally more familiar to the medical profession of this country.

One thing, however, is necessary as a preliminary to the examination of urine, which has not generally been sufficiently considered; that is to say, the relation between the quantity of secretion passed in a given time and the amount of solid matters found in it by analysis. From a medical point of view it is a mere waste of time, generally speaking, to determine the constituents in half-a-pint or so of urine passed at any particular hour of the day or night without

* In a word, whenever c.c. occurs, dm. may be substituted; and in case of using grains for grams, move the decimal point one place to the right; thus 7·0 grams would be changed to 70 grains. Of course it is understood that where grams are taken c.c. must be measured, and with grains dm., the standard solution being the same for both systems.

ascertaining the relation which that quantity, with its constituents, bears to the whole quantity passed during, say, 24 hours; and this is the more necessary, as the amount of fluid secreted varies very considerably in healthy persons; besides this, the analyst should register the colour, peculiarity of smell (if any), consistence, presence or absence of a deposit (if the former, it should be collected for separate analysis, filtered urine only being used in such cases for examination), and lastly its reaction to litmus should be observed.

1. Specific Gravity.

This may be taken by measuring 10 c.c. with an accurate pipette into a tared beaker or flask. The observed weight say is 10·265 gm.; therefore 1026·5 will be the specific gravity, water being 1000. Where an accurate balance, pipette, or weights are not at hand, a good urinometer may be used. These instruments are now to be had with enclosed thermometer and of accurate graduation.

2. Determination of Chlorides (calculated as Sodium Chloride).

This may be done in various ways. Liebig's method is by far the simplest, but the end point is generally so obscure that the liability to error is very great, and therefore the details of the process are omitted. Mohr's method is modified by the use of ammonium in place of potassium nitrate, owing to the solvent effect which the latter has been found to produce on silver chromate. By ignition the ammonia salt is destroyed.

(*a*) **By Silver Nitrate and Chromate Indicator** (Mohr).—10 c.c. of the urine are measured into a thin porcelain capsule, and 1 gm. of pure ammonium nitrate in powder added; the whole is then evaporated to dryness, and gradually heated over a small spirit lamp to low redness till all vapours are dissipated and the residue becomes white*; it is then dissolved in a small quantity of water, and the carbonates produced by the combustion of the organic matter neutralized by dilute acetic acid; a few grains of pure calcium carbonate are then added, to remove all free acid, and one or two drops of solution of potassium chromate.

The mixture is then titrated with $^{N}/_{10}$ silver, as on p. 142.

Each c.c. of silver solution represents 0·005846 gm. of salt, consequently if 12·5 c.c. have been used, the weight of salt in the 10 c.c. of urine is 0·073075 gm., and as 10 c.c. only were taken, the weight multiplied by 10, or what amounts to the same thing, the decimal point moved two places to the right, gives 7·3075 gm. of salt for 1000 c.c. of urine.

If 5·9 c.c. of the urine are taken for titration, the number of c.c. of $^{N}/_{10}$ silver used will represent the number of parts of salt in 1000 parts of urine.

* Dr. Edmunds has called my attent on to the fact that there is great danger of losing chlorine if the ignition is made at a high temperature, and there is no doubt he is right. He prefers to char the urinary residue thoroughly over a spirit lamp, and wash out the chlorides with hot water. The filtered liquid is then available for direct determination with silver and chromate or by the Volhard method.

(*b*) **By Volhard's Method.**—This is a direct determination of Cl by excess of silver and the excess found by ammonium or potassium thiocyanate (p. 145), which gives very good results in the absence of much organic matter, and is carried out as follows :—

10 c.c. of urine are placed in a 100 c.c. flask and diluted to about 60 c.c. 2 c.c. of pure nitric acid and 15 c.c. of standard silver solution (1 c.c. =0·01 gm. NaCl) are then added ; the closed flask is well shaken, and the measure made up to 100 c.c. with distilled water.

The mixture is then passed through a dry filter, and either 70 or 80 c.c. of the clear fluid titrated with standard thiocyanate for the excess of silver, using the ferric indicator described on page 146. The relative strength of the silver and thiocyanate being known, the measure of the former required to combine with the chlorine in the 7 or 8 c.c. of urine is found and calculated into NaCl.

Arnold* carries out this process as follows :—

10 c.c. of urine are mixed with 10 drops to 20 of nitric acid sp. gr. 1·2, 2 c.c. of ferric indicator, and 10 to 15 drops of solution of permanganate to oxidize organic matter. The liquid is then filtered and titrated as described above.

3. Determination of Urea.

Carbamide $CO(NH_2)_2$.

If a solution of urea is mingled with an alkaline solution of sodium hypochlorite or hypobromite, the urea is rapidly decomposed and nitrogen evolved, which can be collected and measured in any of the usual forms of gas apparatus described in the section on gas analysis.

$$\underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Sodium hypobromite.}}{3\,Na\,Br\,O} = \underset{\text{Sodium bromide.}}{3Na\,Br} + 2H_2O + CO_2 + N_2.$$

Test experiments with pure urea have shown that the whole of the nitrogen contained in it is eliminated in this process, with the exception of a constant deficit of 8 per cent. The carbon dioxide set free in the reaction is absorbed by the excess of caustic alkali present, so that nitrogen gas alone is evolved. In the case of urine there are other nitrogenous constituents present, such as uric acid, hippuric acid, and creatinine, which render up a small proportion of their nitrogen in the process, but the quantity so obtained is insignificant, and may be disregarded. Consequently, for all medical purposes, this method of determining urea in urine is sufficiently exact.

In the case of diabetic urines, however, Méhu and others have pointed out that this deficiency is diminished, and if, in addition to the glucose present, cane sugar be also added, it will almost entirely disappear. Méhu† therefore recommends that in the analysis of saccharine urines cane sugar be added to the extent of ten times the amount of urea present, when the difference between the actual and theoretical yield of nitrogen will not exceed 1 per cent.

Russell and West‡ have described a very convenient apparatus

* *Pflüger's Archiv.* **30**, 541. † *Bull. Soc. Chim.* [2] **33**, 410.
‡ *J. C. S.* [2] **12**, 749.

for working the process, which gives very good results in a short space of time. This method has given rise to endless forms of apparatus devised by various operators, including Méhu, Yvon, Dupré, Apjohn, Maxwell Simpson, Doremus, O'Keefe, etc., etc.; the principles of construction are all, however, the same. Those who may wish to construct simple forms of apparatus from ordinary laboratory appliances, will do well to refer to the arrangements of Dupré* or Maxwell Simpson†. The nitrometer, with side flask, and using mercury, is perhaps the best of all for the gasometric determination of urea. Each c.c. of N produced, after correction for temperature, pressure, and moisture, being equal to 0·002913 gm. of urea on the assumption that 92 % is evolved.

The apparatus devised by Russell and West is shown in fig. 58, and may be described as follows :—

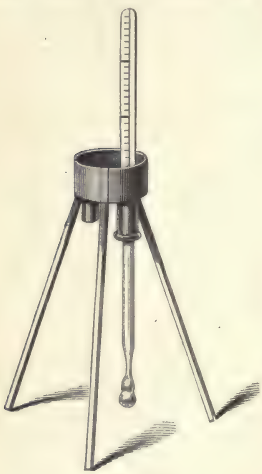


Fig. 58.

The tube for decomposing the urine is about 9 inches long, and about half an inch inside diameter. At 2 inches from its closed end it is narrowed, and an elongated bulb is blown, leaving the orifice at its neck ⅜ of an inch in diameter; the bulb should hold about 12 c.c. The mouth of this tube is fixed into the bottom of a tin tray about 1¾ inch deep, which acts as a pneumatic trough; the tray is supported on legs long enough to allow of a small spirit lamp being held under the bulb tube. The measuring tube for collecting the nitrogen is graduated into cubic centimetres, and is of such size as to fit over the mouth of the decomposing tube; one holding about 40 c.c. is a convenient size. Russell and West have fixed by experiment the proportions, so as to obviate the necessity for correction for pressure and temperature, namely, 37·1 c.c. = 0·1 gm. of urea, since they found that 5 c.c. of a 2 per cent. solution of urea constantly gave 37·1 c.c. of nitrogen at ordinary temperatures and pressures. The entire apparatus can be purchased of most operative chemists for a moderate sum.

Hypobromite Solution.—This is best prepared by dissolving 100 gm. of caustic soda in 250 c.c. of water, and at the time required 25 c.c. of the (cold) solution are mixed with 2·5 c.c. of bromine; this mixture gives a rapid and complete decomposition of the urea. Strong solution of sodium or calcium hypochlorite answers equally well.

Method of Procedure: 5 c.c. of the urine are measured into the bulb-tube, fixed in its proper position, and the sides of the tube washed down with distilled water so that the bulb is filled up to its constriction. A glass rod, having a thin

* *J. C. S.* 1877, 534. † *Ibid.* 538.

band of india-rubber on its end, is then passed down into the tube so as to plug up the narrow opening of the bulb. The hypobromite solution is then poured into the upper part of the tube until it is full, and the trough is afterwards half filled with water.

The graduated tube is filled with water, the thumb placed on the open end, and the tube is inverted in the trough. The glass rod is then pulled out, and the graduated tube slipped over the mouth of the bulb-tube.

The reaction commences immediately, and a torrent of gas rises into the measuring tube. To prevent any of the gas being forced out by the reaction, the upper part of the bulb-tube is slightly narrowed, so that the gas is directed to the centre of the graduated tube. With the strength of hypobromite solution above described, the reaction is complete in the cold in about ten or fifteen minutes; but in order to expedite it, the bulb is slightly warmed. This causes the mixing to take place more rapidly, and the reaction is then complete in five minutes. The reaction will be rapid and complete only when there is considerable excess of the hypobromite present. After the reaction the liquid should still have the characteristic colour of the hypobromite solution.

The amount of constriction in the tube is by no means a matter of indifference, as the rapidity with which the reaction takes place depends upon it. If the liquids mix too quickly, the evolution of the gas is so rapid that loss may occur. On the other hand, if the tube is too much constricted, the reaction takes place too slowly.

The simplest means of supporting the measuring tube is to have the bulb-tube corked into a well, which projects from the bottom of the trough about one inch downwards. The graduated tube stands over the bulb-tube, and rests upon the cork in the bottom of the well. It is convenient to have, at the other end of the trough, another well, which will form a support for the measuring tube when not in use.

To avoid all calculations, the measuring tube is so graduated that the amount of gas read off expresses at once what may be called the percentage amount of urea in the urine experimented upon; *i.e.*, the number of grams in 100 c.c., 5 c.c. being the quantity of urine taken in each case. The gas collected is nitrogen saturated with aqueous vapour, and the bulk will obviously be more or less affected by temperature and pressure. Alterations of the barometer produce so small an alteration in the volume of the gas that it may generally be neglected; *e.g.*, if there are 30 c.c. of nitrogen, the quantity preferred, an alteration of one inch in the height of barometer would produce an error in the amount of urea of about 0·003; but for more exact experiments, the correction for pressure should be introduced.

In the wards of hospitals, and in rooms where the experiments are most likely to be made, the temperature will not vary much from 65° F., and a fortunate compensation of errors occurs with this form of apparatus in these circumstances. The tension of the aqueous vapour, together with the expansion of the gas at this temperature, almost exactly counterbalances the loss of nitrogen in the reaction.

The authors found from experience that 5 c.c. of urine is the most advantageous quantity to employ, as it usually evolves a convenient bulk of gas to experiment with, *i.e.*, about 30 c.c. They have shown that 5 c.c. of a standard solution containing 2 per cent. of

urea evolve 37·1 c.c. of nitrogen, and have consequently taken this as the basis of the graduation of the measuring tube, viz., 37·1 c.c. of the gas as measured represent 0·1 gm. of urea. This bulk of gas is read off at once as 2 per cent. of urea, and in the same way the other graduations on the tube represent percentage amounts of urea.

If the urine experimented with is very rich in urea, so that the 5 c.c. evolve a much larger volume of gas than 30 c.c., then it is best at once to dilute the urine with its own bulk of water ; take 5 c.c. of this diluted urine, and multiply the volume of gas obtained by two.

If the urine contains much albumen, this interferes with the process in so far that it takes a long time for the bubbles of gas to subside before the volume of gas obtained can be accurately read off. It is therefore better in such cases to remove as much as possible of the albumen by heating the urine with two or three drops of acetic acid, filtering, and then using the filtrate in the usual manner.

Another form of apparatus much used in making this determination is that devised by A. W. Gerrard* (fig. 59).

Fig. 59.

It consists of a graduated tube, which is connected with a second tube, serving as a reservoir, by means of india-rubber tubing. The graduated tube is closed at the top by a rubber stopper, through which passes a T tube, one opening of which is fitted with a short piece of flexible tubing closed by a clip, while the other is connected by a second piece of tubing with a bottle fitted with a perforated cork. In making a test, 25 c.c. of the hypobromite solution are measured into this bottle, then a small test-tube containing 5 c.c. of the urine to be tested is carefully placed in it in such a manner as to avoid contact between the urine and the reagent. The bottle and graduated tube are now connected as shown in the figure, the clip opened, and water poured into the reservoir (**c**) until, by suitably adjusting its height, the water stands at the zero-point in the measuring tube and at the same level in the reservoir—taking care that when this is effected the latter contains but little water.

The clip is then closed, and the bottle so tilted that the urine gradually mixes with the hypobromite solution, the bottle being

* *Pharm. Journ.* [3] **15, 464.**

gently shaken to promote the evolution of gas, which commences immediately and is complete in a few minutes. After five (or preferably ten) minutes the reservoir is lowered until the water in it and in the graduated tube stands at exactly the same level, when the volume of gas is read off at once as percentage of urea contained in the urine. If the urine contains more than 3 per cent. of urea, it is necessary to take 2·5 instead of 5 c.c., dilute it with an equal volume of water, and double the result obtained.

4. Determination of Phosphoric Acid (see also p. 307 et seq.).

The principle of this method is fully described at page 307.

The following solutions are required :—

(1) Standard uranium acetate or nitrate. 1 c.c. = 0·005 gm. P_2O_5 (see p. 309).

(2) Standard phosphoric acid (see p. 309).

(3) Solution of sodium acetate (see p. 309).

(4) Solution of potassium ferrocyanide.—About 1 part to 20 of water, freshly prepared.

Method of Procedure : 50 c.c. of the clear urine are measured into a small beaker, together with 5 c.c. of the solution of sodium acetate (if uranium nitrate is used.) The mixture is then warmed in the water-bath, or otherwise, and the uranium solution delivered in from the burette, with constant stirring, so long as a precipitate is seen to form. A small portion of the mixture is then removed with a glass rod and tested as described (p. 309); so long as no brown colour is produced, the addition of uranium may be continued; when the faintest indication of this reaction is seen, the process must be stopped, and the amount of colour observed. If it coincides with the original testing of the uranium solution with a similar quantity of fluid, the result is satisfactory, and the quantity of solution used may be calculated for the total phosphoric acid contained in the 50 c.c. of urine ; if the uranium has been used accidentally in too great quantity, 10 or 20 c.c. of the same urine may be added, and the testing concluded more cautiously. Suppose, for example, that the solution has been added in the right proportion, and 19·2 c.c. used, the 50 c.c. will have contained 0·096 gm. phosphoric acid (= 1·92 per 100). With care and some little practice the results are very satisfactory.

Earthy Phosphates.—The above determination gives the total amount of phosphoric acid, but it may sometimes be of interest to know how much of it is combined with lime and magnesia. To this end 100 or 200 c.c. of the urine are measured into a beaker, and rendered freely alkaline with ammonia ; the vessel is then set aside for ten or twelve hours, for the precipitate of earthy phosphates to settle : the clear liquid is then decanted through a filter, the precipitate brought upon it and washed with ammoniacal water ; a hole is then made in the filter and the precipitate washed through ; the paper moistened with a little acetic acid, and washed into the vessel containing the precipitate, which latter is dissolved in acetic acid (some sodium acetate added if uranium nitrate is used), and the mixture diluted to about 50 c.c. and titrated as before described ; the quantity of phosphoric acid so found is deducted from the total previously determined, and the remainder gives the quantity existing in combination with alkalies.

5. Determination of Sulphuric Acid.

Standard barium chloride.—A quantity of crystallized barium chloride is to be powdered and dried between folds of blotting-

paper. Of this, 30·5 gm. are dissolved in distilled water, and the liquid made up to a litre. 1 c.c. =0·01 gm. of SO_3.

Solution of sodium sulphate.—1 part to 10 of water.

Method of Procedure: 100 c.c. of the urine are poured into a beaker, a little hydrochloric acid added, and the whole placed on a small sand-bath, to which heat is applied. When the solution boils, the barium chloride is allowed to flow in very gradually as long as the precipitate is seen distinctly to increase. The heat is removed, and the vessel allowed to stand, so that the precipitate may subside. Another drop or two is then added, and so on, until the whole of the SO_3 is precipitated. Much time, however, is saved by using Beale's filter, represented in fig. 23. A little of the fluid is thus filtered clear, poured into a test-tube, and tested with a drop from the burette; this is afterwards returned to the beaker, and more of the test solution added, if necessary. The operation is repeated until the precipitation is complete. In order to be sure that too much of the baryta solution has not been added, a drop of the clear fluid is added to the solution of sodium sulphate placed in a test-tube or upon a small mirror (see p. 351). If no precipitate appears, more barium must be added; if a slight cloudiness takes place, the analysis is finished; but if much precipitate is produced, too large a quantity of the test has been used, and the analysis must be repeated.

For instance, suppose that 18·5 c.c. have been added, and there is still a slight cloudiness produced which no longer increases after the addition of another ½ c.c., we know that between 18½ and 19 c.c. of solution have been required to precipitate the whole of the sulphuric acid present, and that accordingly the 100 c.c. of urine contain between 0·185 and 0·19 gm. of SO_3.

6. Determination of Glucose.

Fehling's original method is precisely the same as described on p. 327, but the most suitable methods for urine are Gerrard's cyano-cupric (p. 337), or the Pavy-Fehling.

Process for the Cyano-cupric Solution.—10 c.c. of the clear urine are diluted by means of a measuring flask to 200 c.c. with water, and a large burette filled with the fluid. To 10 c.c. of the cyano-cupric solution prepared as directed (p. 337) are then measured another 10 c.c. of Fehling's copper solution and the liquid brought to boiling; the diluted urine is then delivered cautiously from the burette into the still boiling liquid, and with constant stirring, until the bluish colour has nearly disappeared. The addition of the urine must then be continued more carefully, until the colour is all removed, the burette is then read, and the quantity of sugar in the urine calculated as follows:—

Suppose that 40 c.c. of the diluted urine have been required to reduce the 10 c.c. of copper solution, that quantity will have contained 0·05 gm. of sugar; but, the urine being diluted 20 times, the 40 c.c. represent only 2 c.c. of the original urine; therefore 2 c.c. of it contain 0·05 gm. of glucose, or 25 parts per 1000.

If the Pavy-Felhing solution is used, it is prepared as described on p. 335.

Method of Procedure: 10 c.c. of clear urine are diluted as just described, and delivered cautiously from the burette into 50 or 100 c.c. of the Pavy-Fehling liquid (previously heated to boiling) until the colour is discharged. The calculation is the same as before. 100 c.c. of Pavy-Fehling solution =0·05 gm. glucose.

The ammoniacal fumes are best absorbed by leading an elastic tube from

the reduction flask into a beaker of water ; the end of the tube should be plugged with a piece of solid glass rod, and a transverse slit made in the elastic tube just above the plug. This valve allows the vapours to escape, but prevents the return of the liquid in case of a vacuum.

7. Determination of Uric Acid.

$C_5H_4N_4O_3$.

A method for the accurate determination of this constituent of urine has, up to the present, not been found ; that is to say, although good results may be obtained with chemically prepared pure uric acid, there is no certainty that the same correctness will be attained with the urinary acid as separated in the usual way. The difficulty is caused by the complicated character of the urine itself, and however accurate the process may be with the acid itself in a pure state, it becomes far less reliable when such method is applied to normal or abnormal urine. The precipitation of the acid in combination with some metal, such as silver or copper, carries with it also the so-called alloxuric bases, and the separation by hydrochloric acid contaminates the precipitate with colouring and other matters which militate against its accurate determination with permanganate. I am, however, of the opinion that the latter method is, even now, one of the best for a rapid comparative determination of this constituent.

Method of Procedure : 200 c.c. of the urine are put into an evaporating basin with a few drops of concentrated hydrochloric acid, and evaporated on the water-bath to about half the volume ; it is then transferred to a closely-stoppered flask, together with any slight precipitate which may have formed. 5 c.c. of concentrated hydrochloric acid are then added, and the mixture violently shaken for a few minutes. It is then allowed to settle for half an hour and the liquid passed through a small filter of smooth, hard texture, taking care to pass as little as possible of the sediment on to the filter. About 20 c.c. of cold water are then added to the precipitate in the flask, which is in turn passed through the filter. The filter is then also washed with about the same quantity of water ; a hole is then made at its apex, and the small quantity of adhering precipitate washed into the original flask. Finally about 10 c.c. of concentrated solution of caustic potash (1 : 10) are added to the contents of the flask and slightly warmed until a clear solution is obtained. The mixture is then diluted with about 100 c.c. of cold water, 20 c.c. of dilute sulphuric acid added (1 : 5). and the titration with $^{N}/_{10}$ permanganate carried out in the usual manner.

Another form of the permanganate process is to precipitate the phosphates from 100 c.c. of urine with sodium carbonate. The filtrate is mixed with 5 c.c. of a 4 per cent. solution of copper sulphate and 20 c.c. of a solution containing 10 per cent. each of Rochelle salt and sodium thiosulphate. The precipitate so formed is filtered off and well washed with distilled water, then transferred to a flask with about 400 c.c. of water, 5 c.c. of sulphuric acid added, and the uric acid titrated with permanganate.

No absolute weight of uric acid can be calculated from the results, but Mohr assumes that each c.c. of $^{N}/_{10}$ permanganate $= 0·0075$ gm. of uric acid* ; the process may, however, be made available for

* This figure has been verified by F. G. Hopkins (Allen's *Chemistry of Urine*, p. 171).

pathological purposes by comparing the results from time to time with the urine from the same person.

The following method has a good claim to accuracy as regards the actual amount of uric acid present in any given specimen of urine, but is tedious. It is based on the fact that an alkaline solution of uric acid reduces Fehling solution in the same way as glucose. The method is worked out by E. Riegler*, who found that an average of many experiments gave 0·8 gm. of reduced copper for 1 gm. of uric acid. The acid is first separated from the urine as ammonium urate by Hopkins's method :—

METHOD OF PROCEDURE : 200 c.c. of urine are mixed with 10 c.c. of a saturated solution of sodium carbonate, allowed to stand for half an hour, and filtered from the precipitated phosphates. The precipitate is washed with 50 c.c. of hot water, and to the filtrate and wash-water 20 c.c. of a saturated solution of ammonium chloride added. The liquid is well stirred, and after five hours filtered, preferably through a Schleicher and Schüll filter, No. 597, 11 cm. The precipitate of ammonium urate is washed with 50 c.c. of water, and then introduced by means of a jet from a washing-bottle into a 300 c.c. beaker. Several drops of potash are added to clear the liquid, then 60 c.c. of Fehling's solution, and the whole well stirred. The beaker is then heated on wire gauze until the liquid boils, the boiling being continued for five minutes. When the precipitate has subsided, the liquid is filtered through a small tough filter (Schleicher and Schüll, No. 590, 9 cm.), the precipitate well washed, and dissolved in 20 c.c. of nitric acid (sp. gr. 1·1), the filter being washed with 60 c.c. of water.

To this solution dry powdered sodium carbonate is added little by little until there is a permanent turbidity. The liquid is then cleared by the cautious addition of dilute sulphuric acid, and made up to 100 c.c. 25 c.c. of this are placed in a 100 c.c. flask, 1 gm. of potassium iodide in 10 c.c. of water added, allowed to stand for ten minutes, then titrated with standard thiosulphate solution (1 c.c. =0·002 gm. uric acid), using starch as the indicator. To the total amount of uric acid found in the 200 c.c. of urine, an additional 0·020 gm. should be added to allow for the solubility of the ammonium urate in urine.

The standard thiosulphate solution is made by diluting 126 c.c. of $^{N}/_{10}$ solution to 500 c.c. The reaction is :—

$$2Cu(NO_3)_2 = 4KI + Cu_2I_2 + 4KNO_3 + I_2.$$

The reduced cuprous oxide may also be weighed directly or reduced to metallic copper, as in the determination of sugar. In the latter case the amount of copper, multiplied by the factor 1·25, gives the corresponding amount of uric acid.

E. H. Bartley† points out with reason that the object for which the determination of uric acid is generally made does not require extreme accuracy. The most acceptable process ought to be one which will give consistent results and which can be quickly accomplished, and though not absolutely exact is nevertheless comparatively so. The method proposed by Bartley is based to some extent upon previous ones by Salkowski, Haycraft, etc., that is to say, the uric acid is precipitated from the urine by silver nitrate in the presence of an excess of ammoniacal magnesia mixture.

METHOD OF PROCEDURE : To 50 or 100 c.c. of the clear urine add 5 c.c. of ordinary magnesia mixture such as is used for phosphates, and about 10 c.c. of

* *Z. A. C.* 1896, 31. † *J. Am. C. S.* 1897, 649.

ammonia of sp. gr. 0·96,—this must be in excess. Warm the mixture on the water-bath and add from a burette $^N/_{50}$ silver nitrate until a drop of the filtrate when brought into contact with a drop of weak sodium sulphide solution on a white plate shows a dark ring or cloud. The filtration can be carried out with Beale's filter (fig. 23) or a dropping pipette can be used, the end of which is tied over with cotton wool. The clear liquid only must be tested. Each c.c. of silver solution represents 0·00336 gm. of uric acid, and the number of c.c. used (less one half of a c.c. for each 50 c.c. of urine) when multiplied by this factor will give the amount of uric acid in the urine examined. The half c.c. is deducted because it takes that amount of silver solution to give the colour with 50 c.c. of plain water.

As soon as the process is complete the precipitate settles freely, and it is advisable to test a drop of the clear solution again. The ending can also be checked by adding a drop of the silver to the clear supernatant liquid to see whether a cloudiness appears.

There being no excess of silver in the hot liquid at any time there can be no reduction of the silver. If after the titration is complete the mixture be allowed to cool to ordinary temperature it will be found that 1 to 3 c.c. more silver will be required to give the colour test, and this Bartley attributes to the precipitation of xanthin bases by the silver in a cold solution, which does not take place when the solution is heated.

J. W. Tunnicliffe and O. Rosenheim* publish a method which may be rapidly performed when once the uric acid is obtained as ammonium salt by Hopkins's process. The crystals obtained by decomposing the urate with HCl are washed free from the latter on a small filter with repeated small proportions of water to remove all HCl, the uric acid is then rinsed into a flask with 20 or 30 c.c. of hot water, through a hole made in the filter, and is ready for titration.

Method of Procedure: This depends on the fact that piperidine combines with uric acid in molecular proportions (4·25 gm. of base equal 8·4 gm. of acid) to form a soluble salt. A $^N/_{20}$ solution of the former is prepared by dissolving about 4·2 gm. of piperidine in 1 litre of water, standardizing it on hydrochloric acid of equivalent strength, phenolphthalein being used as indicator. The sample of uric acid separated from ammonium urate as above described is suspended in water, heated nearly to the boiling-point, and the reagent run in; neutrality being shown either by the liquid becoming clear or by the use of phenolphthalein as before. Although the solubility of the urate at 15° is 5·3 per cent., it is better to employ hot solutions; and there is no danger of losing any piperidine by volatilization, as the reaction is instantaneous.

Dr. Edmunds sends me the following remarks as to the determination of uric acid.

1. Chemical uric acid differs entirely in its habitudes from urinary uric acid. Its crystalline form is always uniform as chemical uric acid—colourless—and quite different from urinary uric acid, which, as got from urine, is always coloured yellow-brown, and is protean in its crystalline forms.

2. The problem of titrating chemical uric acid—or pure uric acid—is not quite the same as that of titrating the uric acid in urine. I am not yet able to say in what the difference consists, and I have often crystallized pure uric acid out of iron and other solutions, but have never been able to colour uric acid, nor to get it to crystallize again like urinary uric acid. The only way in which I have succeeded is to add an alkaline solution of chemical urate of potash to a urine out of which I had precipitated all its uric acid with HCl. In that way I found that the uric acid took up from the urine something which gave it the colouration and the protean crystalline form of urinary uric acid. I have thought

* *Centralbl. Physiol.* 1897. **11**. 434.

that urinary uric acid is really a combination of chemical uric acid with some animal base or colouration of urine.

3. To purify urinary uric acid it should be dissolved (and thrown out by dilution) in H_2SO_4 three successive times. In titrating this with permanganate I am not prepared to give you the reaction, but the practical point is that, as the permanganate goes in by drops, it is instantly decolourized as long as there is any uric acid present, and the end-point is marked quite distinctly (if you are on the look out for it) by a certain hang or hesitation in the decolourization of the permanganate.

4. Fokker's process, as modified by Hopkins, is, I think, the best. The saturation with *pure* NH_4Cl of an acid urine (which should be freshly passed and filtered at 120°) throws out all the uric acid as ammonium urate. This is well set out in Allen's *Chemistry of Urine*, p. 168. But much of the work does not say whether the processes have been worked out on the chemical uric acid or on the natural uric acid, freshly obtained from urine. What we have to deal with in medicine is that coloured protean crystalline substance which comes out constantly from urines on adding pure strong HCl and setting aside for forty-eight hours. That is what we get in the uric acid diathesis, in gout, and in calculi.

For the determination of uric acid I set aside 100 c.c. of fresh urine, filtered at about 120° F., and acidify it with 5 % of pure strong hydrochloric acid. At the end of forty-eight hours a deposit of uric acid will be seen at the bottom of the tube, and from this a very good idea is gained of the amount of uric acid in the urine. If closer quantification be wanted, the uric acid is collected on a small fine filter paper, washed with a few centimetres of ice-cold distilled water, then dried and weighed, with deduction for the filter paper, and with addition for the uric acid dissolved in the 105 c.c. of acid urinary mother-liquor. The amount of uric acid contained in the 105 c.c. of liquid would depend upon the temperature before and at the time of filtration. At 33° F. it would contain only some 2 mgm., at 68° F. it would contain 6 mgm., at 212° F. it would contain 62·5 mgm.

8. Determination of Lime and Magnesia.

METHOD OF PROCEDURE: 100 c.c. of the urine are precipitated with ammonia, the precipitate re-dissolved in acetic acid, and sufficient ammonium oxalate added to precipitate all the lime present as oxalate. The precipitate is allowed to settle in a warm place, then the clear liquid passed through a small filter, the precipitate brought upon it, washed with hot water, the filtrate and washings set aside, then the precipitate, together with the filter, pushed through the funnel into a flask, some sulphuric acid added, the liquid freely diluted, and titrated with permanganate, precisely as on p. 172; each c.c. of $^{N}/_{10}$ permanganate required represents 0·0028 gm. of CaO.

Or the following method may be adopted :—

The precipitate of calcium oxalate, after being washed, is dried, and together with the filter, ignited in a platinum or porcelain crucible, by which means it is converted into a mixture of calcium oxide and carbonate. It is then transferred to a flask by the aid of the washing-bottle, and an excess of $^{N}/_{10}$ nitric acid delivered in with a pipette. The amount of acid, over and above what is required to saturate the lime, is found by $^{N}/_{10}$ caustic alkali, each c.c. of acid being equal to 0·0028 gm. of CaO.

In examining urinary sediment or calculi for calcium oxalate, it is first treated with caustic potash to remove uric acid and organic matter, then dissolved in sulphuric acid, freely diluted, and titrated with permanganate ; each c.c. of $^{N}/_{10}$ solution represents 0·0054 gm. of calcium oxalate.

Magnesia.—The filtrate and washings from the precipitate of

calcium oxalate are evaporated on the water-bath to a small bulk, then made alkaline with ammonia, sodium phosphate added, and set aside for 8 or 10 hours in a cool place so that the magnesia may separate as ammonio-magnesium phosphate. The supernatant liquid is then passed through a small filter, the precipitate brought upon it, washed with ammoniacal water in the cold, and dissolved in acetic acid, then titrated with uranium solution, as on p. 309; each c.c. of solution required represents 0·002815 gm. of magnesia.

9. Ammonia.

The method hitherto applied to the determination of free ammonia and its salts in urine is that of Schlösing, which consists in placing a measured quantity of the urine, to which milk of lime is previously added, under an air-tight bell-glass, together with an open vessel containing a measured quantity of standard acid. In the course of from 24 to 36 hours all the ammonia will have passed out of the urine into the acid, which is then titrated with standard alkali to find the amount of ammonia absorbed.

One great objection to this method is the length of time required, since no heating must be allowed, urea evolving free ammonia when heated with alkali. There is also the uncertainty as to the completion of the process; and if the vessel be opened before the absorption is complete, the analysis is spoiled.

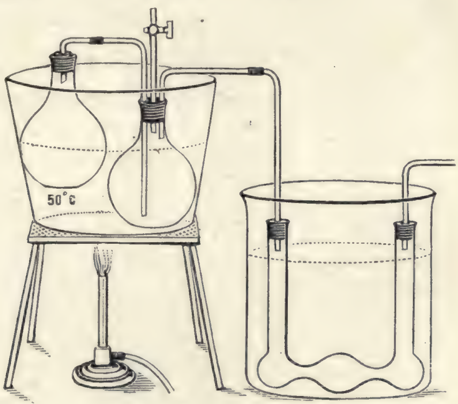


Fig. 60.

Another method which gives good results, and occupies only a short time, has been devised by C. Wurster*. The apparatus necessary for it is shown in Fig. 60. The principle of the method is the same as Schlösing's, but the liberation of ammonia is hastened by increase of temperature under reduced atmospheric pressure.

As is well-known, urea is decomposed when urine is boiled with caustic alkali or alkaline earth into ammonium carbonate, but if the

* *Centralblatt. f. Physiologie*, Dec. 1887.

operation is carried on at 50° C. and in a vartial vacuum, practically no such decomposition occurs. In fact a solution of artificial urea gives off no ammonia, even when evaporated nearly to dryness with b rium, calcium, or magnesium hydrate, in a vacuum at 50° C. Owing to the production of much froth when urine is heated with baryta or lime under reduced pressure, one flask for distillation is not enough, although the frothing may be reduced to some extent by adding some high-boiling hydro-carbon such as paraffin or toluol; but a much safer plan is to use two flasks as shown in the figure, or by using only a small quantity of urine two good-sized boiling tubes will suffice. The boiling-flask dips a small way into the water and the second flask rests on the bottom of the bath; the tube with stop-cock or burette clip, which simply enters below the rubber stopper in this flask, allows air to enter when the operation is ended so as to clear out every trace of ammonia. The absorption tube containing standard acid must have rather long side tubes, and the whole must be immersed in a beaker of cold water. The delivery end of this tube is connected with an efficient water pump, and of course all connections must be perfectly tight.

METHOD OF PROCEDURE: 10 to 20 c.c. of the urine with 10 to 20 c.c. of saturated barium hydrate or lime solution, with a little water, are placed in the distilling flask, and the water-bath gradually heated up to 50° C., and the whole apparatus is covered with a cloth to avoid regurgitation from cold air. When two-thirds of the distilling liquid have passed over, the ammonia will have all been absorbed by the standard acid, and the valve or stop-cock may be opened while the pump is still working so as to clear away the last traces of vapour.

The method can be used for liquids other than urine.

The following method is available in some cases :—

When a solution containing salts of ammonia is mixed with a measured quantity of free fixed alkali of known strength, and boiled until ammoniacal gas ceases to be evolved, it is found that the resulting liquid has lost so much of the free alkali as corresponds to the ammonia evolved (p. 76) ; that is to say, the acid which existed in combination with the ammonia in the original liquid has simply changed places, taking so much of the fixed alkali (potash or soda) as is equivalent to the ammonia it has displaced. In the case of urine being treated in this way, the urea will also be decomposed into free ammonia, but happily in such a way as not to interfere with the determination of the original amount of ammoniacal salts. The decomposition is such that, while free ammonia is evolved from the splitting up of the urea, carbonate of fixed alkali (say potash) is formed in the boiling liquid, and, as this reacts as alkaline as though it were free potash, it does not interfere in the slightest degree with the determination of the original ammonia.

METHOD OF PROCEDURE: 100 c.c. of the urine are exactly neutralized with $N/10$ soda or potash, as for the determination of free acid; it is then put into a flask capable of holding five or six times the quantity; 10 c.c. of normal alkali added, and the whole brought to boiling, taking care that the abundant froth which is at first formed does not come over. After a few minutes this subsides,

and the boiling proceeds quietly. When all ammoniacal fumes are dissipated, the lamp is removed, and the flask allowed to cool slightly; the contents then emptied into a beaker, and normal nitric acid delivered in from the burette with constant stirring, until a fine glass rod or small feather dipped in the mixture and brought in contact with violet-coloured litmus paper produces neither a blue nor a red spot. The number of c.c. of normal acid are deducted from the 10 c.c. of alkali, and the rest calculated as ammonia. 1 c.c. of normal alkali = 0·017 gm. of ammonia.

It must be borne in mind that the plan just described is not applicable to urine which has already suffered decomposition by age or other circumstances so as to contain ammonium carbonate; in this case it would be preferable to adopt the Wurster or Schlösing method.

10. Determination of Free Acid.

The acidity of normal urine is doubtless due to various substances, among the most prominent of which appear to be acid sodium phosphate ($Na\,H_2\,PO_4$) and lactic acid. Other free organic acids are probably in many cases present. In these circumstances, the degree of acidity cannot be placed to the account of any particular body; nevertheless, it is frequently desirable to ascertain its amount, which is best done as follows:—

100 c.c. of urine are measured into a beaker, and $^N/_{50}$ alkali delivered in from a small burette, until a thin glass rod or feather, moistened with the mixture and streaked across some well-prepared violet litmus paper, produces no change of colour; the degree of acidity is then registered as being equal to the quantity of alkali used.

Accurate results are obtained by the method of Gautier, in which the urine is made alkaline by standard caustic soda in known quantity, and the phosphates and other salts precipitated by neutral barium chloride. The liquid is made up to a definite volume with distilled water, and when settled an aliquot portion is titrated with standard acid and phenolphthalein.

11. Determination of Albumen.

The accurate determination of this substance is difficult and troublesome. The best process is perhaps that recommended by Méhu.

Method of Procedure: 100 c.c. of the urine are slightly acidified with acetic acid, 2 c.c. of strong nitric acid are added and the mixture thoroughly agitated. 10 c.c. of a mixture of crystallized carbolic acid 1 part, acetic acid 1 part, and alcohol 2 parts are then added, and the whole well stirred for a few minutes. The precipitate is collected on a small filter and washed with a cold aqueous solution of 4 per cent. of carbolic acid; when fully washed the filter is dried, and together with the paper the precipitate is treated by the Kjeldahl process, and the nitrogen obtained is multiplied by 6·3 for albumen. The presence of sugar or much saline matter does not affect the accuracy of results.

12. Determination of Soda and Potash.

50 c.c. of urine are mixed with the same quantity of baryta solution, allowed to stand a short time, and filtered; then 80 c.c. (= 40 c.c. urine) measured

into a platinum dish and evaporated to dryness in the water-bath ; the residue is then ignited to destroy all organic matter, and when cold dissolved in a small quantity of hot water, ammonium carbonate added so long as a precipitate is produced, filtered through a small filter, the precipitate washed, the filtrate acidified with hydrochloric acid and evaporated to dryness, then cautiously heated to expel all ammoniacal salts. The residue is then treated with a little water and a few drops each of ammonia and ammonium carbonate, filtered, the filter thoroughly washed, the filtrate and washings received into a tared platinum dish, then evaporated to dryness, ignited, cooled, and weighed.

By this means the total amount of mixed sodium and potassium chlorides is obtained. The proportion of each is found by titrating for the chlorine as on p. 142, and calculating as directed on page 144, or the soda may be determined direct by Fenton's method (p. 65).

13. Determination of Total Nitrogen.

This can now be easily accomplished by Kjeldahl's method (p. 83) and is especially serviceable, since it has been found that the results of the titration method for urea by Liebig's process, either in its original way or by subsequent modifications, cannot give the true data for calculating the total nitrogen in any given specimen of urine.

Method of Procedure : 5 c.c. of urine of average concentration are measured into a flask holding about 300 c.c., together with 10 c.c. of sulphuric acid, then gradually heated to boiling, and the heat continued until all vapour and gases are given off and the fluid possesses a clear yellow tint. 25 to 30 minutes generally suffice unless sugar is present in tolerable quantity, in which case mercuric oxide and potassium sulphate must be used, and perhaps more sulphuric acid. The flask is then suffered to cool, the liquid diluted, and distilled with caustic soda and zinc as described on p. 87.

ANALYSIS OF NATURAL WATERS AND SEWAGE.

THE analysis of natural waters and sewage has from an early period received the attention of chemists, but for long no methods of examination were produced which could be said to satisfy the demands of those interested in the subject from various points of view, The researches of Frankland and Armstrong, Miller, Wanklyn, Tidy, Crookes, Dewar, and others, have, however, now brought the whole subject into a more satisfactory form, so that it may fairly be said that, as regards accuracy of chemical processes or interpretation of results from a chemical and sanitary point of view, very little addition is required. Considerable space will be devoted to the matter here; and as most of the processes are now volumetric, and admit of ready and accurate results, the general subject naturally falls within the scope of this work. Care has been taken to render the treatment of the matter practical and trustworthy.

The bacteriological examination of waters has now been largely developed and undoubtedly is of the greatest importance, especially with the filtered waters derived from rivers, lakes, and other sources liable to be contaminated with unoxidized surface or drainage impurities. This book has, however, nothing to describe but chemical methods, and therefore no further mention of bacterial investigation will be made.

THE PREPARATION OF REAGENTS.

A. Reagents required for the Determination of Nitrogen present as Ammonia, Free and Saline, and Albuminoid.

(i) **Nessler's Solution.**—Dissolve 62·5 gm. of potassium iodide in about 250 c.c. of distilled water, set aside a few c.c. and add gradually to the larger part a cold saturated solution of mercuric chloride (of which about 500 c.c. will be required) until the mercuric iodide precipitated ceases to be redissolved on stirring. When a permanent precipitate is obtained, restore the reserved potassium iodide so as to redissolve it, and continue adding mercuric chloride very gradually until a slight precipitate remains undissolved. (The small quantity of potassium iodide is set aside merely to enable the mixture to be made rapidly without danger of adding an excess of mercury.)

Next dissolve 150 gm. of solid potassium hydrate (that usually sold in sticks or cakes) in 150 c.c. of distilled water, allow the solution to cool, add it gradually to the above solution, and make up with distilled water to one litre.

On standing, a brown precipitate is deposited, and the solution becomes clear, and of a pale greenish-yellow colour. It is ready for use as soon as it is perfectly clear, and should be decanted into a smaller bottle as required. The reagent improves on keeping.

(ii) **Standard solution of ammonium chloride.**—Dissolve 1·9093 gm. of pure dry ammonium chloride in a litre of distilled water; of this take 100 c.c., and make up to a litre with distilled water. The latter solution will contain ammonia corresponding to 0·00005 gm. of nitrogen in each c.c. In use it should be measured from a narrow burette of 10 c.c. capacity divided into tenths, or from a 1 c.c. pipette.

[If it is desired to determine "*ammonia*" rather than "*nitrogen as ammonia*" take 1·5708 gm. of ammonium chloride instead of 1·9093 gm.; 1 c.c. will then correspond to 0·00005 gm. of ammonia (NH_3)].

(iii) **Sodium carbonate.**—Heat anhydrous sodium carbonate in a platinum crucible for about an hour, taking care not to fuse it. While still warm rub it in a clean mortar so as to break any lumps which may have been formed, and transfer to a clean dry wide-mouthed stoppered bottle.

(iv) **Water free from Ammonia.**—If, when 1 c.c. of Nessler's solution (**A.** i) is added to 100 c.c. of distilled water in a glass cylinder, standing on a white surface (see Determination of Ammonia), no trace of a yellow tint is visible after five minutes, the water is sufficiently pure for use. As, however, this is rarely the case, the following process must usually be adopted. Distil from a large glass retort (or better, from a copper or tin vessel holding 15—20 litres) ordinary distilled water which has been rendered distinctly alkaline by addition of sodium carbonate. A glass Liebig condenser or a clean tin worm should be used to condense the vapour; it should be connected to the still by a short india-rubber joint. Test the distillate from time to time with Nessler's solution, as above described, and when free from ammonia collect the remainder for use. The distillation must not be carried to dryness. Ordinary water may be used instead of distilled water, but it occasionally continues for some time to give off traces of ammonia by the slow decomposition of the organic matter present in it.

J. Barnes* has pointed out that distilled water can be completely freed from ammonia by adding a little bromine and boiling for a few minutes. More rapid is the action of alkaline hypobromite in the cold. Enough bromine is added to the water to give it a perceptible tint, and then a drop of sodium hydroxide solution; after ten minutes a little potassium iodide is added to remove the undecomposed hypobromite, and the water is then fit for use in the determination of ammonia by Nessler's test.

(v) **Alkaline Permanganate Solution.**—Dissolve 200 grams of stick potash in water in a large porcelain dish and add a solution of 8 grams of potassium permanganate in water, using 1100 c.c. altogether. Boil rapidly until concentrated to about 900 c.c., add about 200 c.c. of hot distilled water, and continue boiling till the volume is reduced to a litre. When cool pour at once into a bottle. Every fresh lot of solution made should be carefully tested before being used.

* *J. S. C. I.* 1896, **15**, 254–255.

B. Reagents required for the Determination of Organic Carbon and Nitrogen.

(i) **Water free from Ammonia and Organic Matter.**—Distilled water to which 1 gm. of potassium hydrate and 0·2 gm. of potassium permanganate per litre have been added, is boiled gently for about twenty-four hours in a similar vessel to that used in preparing water free from ammonia (**A.** iv), a reflux condenser being so arranged as to return the condensed water. At the end of that time the condenser is adjusted in the usual way, and the water carefully distilled, the distillate being tested at intervals for ammonia, as in preparing **A.** iv. When ammonia is no longer found the remainder of the distillate may be collected, taking care to stop short of dryness. The neck of the retort or still should point slightly upwards, so that the joint which connects it with the condenser is the highest point. Any particles carried up mechanically will then run back to the still, and not contaminate the distillate. The water thus obtained should then be rendered slightly acid with sulphuric acid, and re-distilled from a clean vessel for use, again stopping short of dryness.

(ii) **Solution of sulphurous acid.**—Sulphurous anhydride is prepared by the action of pure sulphuric acid upon clippings of clean metallic copper, which have been digested in the cold with concentrated sulphuric acid for twenty-four hours and then washed with water. The gas is made to bubble through water to remove impurities mechanically carried over, and then conducted into water free from ammonia and organic matter (**B.** i) until a saturated solution is obtained.

(iii) **Solution of hydrogen sodium sulphite.**—Sulphurous anhydride, prepared and washed as above, is passed into a solution of sodium carbonate made by dissolving ignited sodium carbonate (**A.** iii) in water free from ammonia and organic matter (**B.** i), The gas is passed until carbonic anhydride ceases to be evolved.

(iv) **Solution of ferrous chloride.**—Pure crystallized ferrous sulphate is dissolved in water, precipitated by sodium hydrate, the precipitate well washed (using pure water **B.** i for the last washings) and dissolved in the smallest possible quantity of pure hydrochloric acid. Two or three drops must not contain an appreciable quantity of ammonia. It is convenient to keep the solution in a bottle with a ground glass cap instead of a stopper, so that a small dropping tube may be kept in it always ready for use.

(v) **Cupric oxide.**—Prepared by heating to redness with free access of air, on the hearth of a reverberatory furnace or in a muffle, copper wire cut into short pieces, or copper sheets cut into strips. That which has been made by calcining the nitrate cannot be used, as it appears to be impossible to expel the last traces of nitrogen. After use, the oxide should be extracted by breaking the combustion tube, rejecting the portion which was mixed with the substance

examined. As soon as a sufficient quantity has been recovered, it should be recalcined. This is most conveniently done in an iron tube about 30 mm. in internal diameter, and about the same length as the combustion furnace. One end should be closed with a cork, the cupric oxide poured in, the tube placed in the combustion furnace (which is tilted at an angle of about 15°, so as to produce a current of air), the cork removed, and the tube kept at a red heat for about two hours. In a Hofmann's gas furnace, with five rows of burners, two such tubes may be heated at the same time if long clay burners are placed in the outer rows, and short ones in the three inner rows. If the furnace has but three rows of burners, a rather smaller iron tube must be used. When cold, the oxide can easily be extracted, if the heat has not been excessive, by means of a stout iron wire, and should be kept in a clean dry stoppered bottle. Each batch thus calcined should invariably be assayed by filling with it a combustion tube of the usual size, and treating it in every respect as an ordinary combustion. It should yield only a very minute bubble of gas, which should be almost wholly absorbed by potassium hydrate. (The quantity of CO_2 found should not correspond to more than 0·00005 gm. of C, otherwise the oxide must be recalcined). The finer portions of the oxide should, after calcining, be sifted out by means of a sieve of clean copper gauze, and reserved for use as described hereafter.

New cupric oxide as obtained from the reverberatory furnace should be assayed, and if not sufficinetly pure, as is most usually the case, calcined as above described, and assayed again.

(vi) **Metallic copper.**—Fine copper gauze is cut into strips about 80 mm. wide, and rolled up as tightly as possible on a copper wire so as to form a compact cylinder 80 mm. long. This is next covered with a tight case of moderately thin sheet copper, the edges of which meet without overlapping. The length of the strip of gauze, and the consequent diameter of the cylinder, must be so regulated that it will fit easily, but not too loosely, in the combustion tubes. A sufficient number of these cylinders being prepared, a piece of combustion tube is filled with them, and they are heated to redness in the furnace, a current of atmospheric air being passed through them for a few minutes in order to burn off organic impurity, and coat the copper gauze superficially with oxide. A current of hydrogen, dried by passing through strong sulphuric acid, is then substituted for the air, and a red heat maintained until hydrogen issues freely from the end of the tube. It is then allowed to cool, the current of hydrogen being continued, and when cold the copper cylinders are removed, and kept in a stoppered bottle. After being used several times they must be heated in a stream of hydrogen as before, and are then again ready for use. The heating in air need not be repeated.

(vii) **Solution of potassium dichromate.**—This is used as a test for and to absorb sulphurous anhydride which may be present in

the gas obtained by combustion of the water residue. It should be saturated, and does not require any special attention. The yellow neutral chromate may also be used, but must be rendered slightly acid, lest it should absorb carbonic as well as sulphurous anhydride.

(viii) **Solution of potassium hydrate.**—A cold saturated solution, made by dissolving stick potash in distilled water.

(ix) **Solution of pyrogallic acid.**—A cold saturated solution, made by dissolving in distilled water solid pyrogallic acid obtained by sublimation.

(x) **Solution of cuprous chloride.**—A saturated solution of cupric chloride is rendered strongly acid with hydrochloric acid, a quantity of metallic copper introduced in the form of wire or turnings, and the whole allowed to stand in a closely stoppered bottle until the solution becomes colourless.

(xi) **Oxygen.**—Blow a bulb of about 30 c.c. capacity at the end of a piece of combustion tube, and draw out the tube so that its internal diameter for a length of about 30 mm. is about 3 mm. This is done in order that the capacity of the apparatus apart from the bulb may be as small as possible. Cut the tube at the wide part about 10 mm. from the point at which the narrow tube commences, thus leaving a small funnel-shaped mouth. Then introduce, a little at a time, dried, coarsely powdered, potassium chlorate until the bulb is full. Cut off the funnel, and, at a distance of 100 mm. from the bulb, bend the tube at an angle of 45°, and at 10 mm. from the end bend it at right-angles in the opposite direction. It then forms a retort and delivery tube in one piece, and must be adjusted in a mercury trough in the usual manner, taking care that the end does not dip deeper than about 20 mm. below the surface, as otherwise the pressure of so great a column of mercury might destroy the bulb when softened by heat. On gently heating, the potassium chlorate fuses and evolves oxygen. The escaping gas is collected in test tubes about 150 mm. long and 20 mm. in diameter, rejecting the first 60 or 80 c.c., which contain the nitrogen of the air originally in the bulb retort. Five or more of these tubes, according to the quantity of oxygen required, are collected and removed from the mercury trough in very small beakers, the mercury in which should be about 10 mm. above the end of the test tube. Oxygen may be kept in this way for any desired length of time, care being taken, if the temperature falls considerably, that there is sufficient mercury in the beaker to keep the mouth of the test tube covered. About 10 c.c. of the gas in the first tube collected is transferred by decantation in a mercury trough to another tube, and treated with potassium hydrate and pyrogallic acid, when—if after a few minutes it is absorbed, with the exception of a very small bubble—the gas in that and the remaining tubes may be considered pure. If not, the first tube is rejected, and the second tested in the same way, and so on.

(xii) **Hydrogen metaphosphate.**—The glacial hydrogen metaphosphate, usually sold in sticks, is generally free from ammonia, or very nearly so. A solution should be made containing about 100 gm. in a litre. It should be so far free from ammonia that 10 c.c. do not contain an appreciable quantity.

(xiii) **Calcium phosphate.**—Prepared by precipitating common disodium phosphate with calcium chloride, washing the precipitate with water by decantation, drying and heating to redness for an hour.

C. Reagents required for the Determination of Nitrogen present as Nitrates and Nitrites (Crum's Process).

(i) **Concentrated sulphuric acid.**—This must be free from nitrates and nitrites.

(ii) **Potassium permanganate.**—Dissolve about 10 gm. of crystallized potassium permanganate in a litre of distilled water.

(iii) **Sodium carbonate.**—Dissolve about 10 gm. of dry, or an equivalent quantity of crystallized, sodium carbonate, free from nitrates, in a litre of distilled water.

For the Determination of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, but little Organic Nitrogen.

(iv) **Metallic aluminium.**—As thin foil.

(v) **Solution of sodium hydrate.**—Dissolve 100 gm. of stick soda in a litre of distilled water; when cold, put it in a tall glass cylinder, and introduce about 100 sq. cm. of aluminium foil, which must be kept at the bottom of the solution by means of a glass rod. When the aluminium is dissolved, boil the solution briskly in a porcelain basin until about one-third of its volume has been evaporated, allow to cool, and make up to its original volume with water free from ammonia. The absence of nitrates is thus ensured.

(vi) **Broken pumice.**—Clean pumice is broken in pieces of the size of small peas, sifted free from dust, heated to redness for about an hour, and kept in a closely stoppered bottle.

(vii) **Hydrochloric acid free from ammonia.**—The acid sold as "pure for analysis" is nearly always quite free from ammoniacal contamination. Only 2 or 3 drops are required for each experiment.

For the Determination of Nitrites by Griess's Process.

(viii) **Meta phenylene-diamine.**—A half per cent. solution of the base in very dilute sulphuric or hydrochloric acid. The base alone is not permanent. If too highly coloured, it may be bleached by pure animal charcoal.

(ix) **Dilute sulphuric acid.**—One volume of acid to two of water.

(x) **Standard potassium or sodium nitrite.**—Dissolve 0·405 gm. of pure silver nitrite in boiling distilled water, and add pure potassium or sodium chloride till no further precipitate of silver chloride is formed. Make up to a litre; let the silver chloride settle, and dilute 100 c.c. of the clear liquid to a litre. It should be kept in small stoppered bottles completely filled, and in the dark.

$$1 \text{ c.c.} = 0·01 \text{ mgm. } N_2O_3.$$

(By using 1·100 gm. of silver nitrites instead of 0·405 gm.

$$1 \text{ c.c.} = 0·01 \text{ mgm. nitrogen.})$$

The colour produced by the reaction of nitrous acid on meta-phenylene-diamine is triamidoazo-benzene, or "Bismarck brown."

D. Reagents required for the Determination of combined Chlorine.

(i) **Standard solution of silver nitrate.**—Dissolve 2·4 grams of recrystallized silver nitrate in a litre of distilled water and standardize against a solution of pure sodium chloride containing 0·8243 gm. per litre (1 c.c. = 0·0005 gm. chlorine). 1 c.c. silver nitrate solution = 0·0005 gm. Cl, or when 50 c.c. of water are titrated, 1 c.c. = 1 part of combined chlorine per 100,000.

(ii) **Solution of potassium chromate.**—A strong solution of pure neutral potassium chromate free from chlorine. It is most conveniently kept in a bottle similar to that used for the solution of ferrous chloride (B iv).

E. Reagents required for determination of Hardness by Clark's method.

(i) **Standard solution of calcium chloride.**—Dissolve in dilute hydric chloride, in a platinum dish, 0·2 gm. of pure crystallized calcite, adding the acid gradually, and having the dish covered with a glass plate, to prevent loss by spirting. When all is dissolved, evaporate to dryness on a water-bath, add a little distilled water, and again evaporate to dryness. Repeat the evaporation several times to ensure complete expulsion of hydric chloride. Lastly, dissolve the calcium chloride in distilled water, and make up to one litre.

$$50 \text{ c.c. correspond to } 0·01 \text{ gm. } CaCO_3.$$

(ii) **Standard solution of potassium soap.**—Weigh out 50 grams of commercial oleic acid in a beaker and add 100 c.c. of an alcoholic potash solution made by dissolving 20 grams of stick potash in 180 c.c. of *industrial* methylated spirit, and continue adding the same solution from a burette till a drop of the oleate just gives a red colour with phenolphthalein spotted on a white plat —about

10 c.c. more being required. Measure the solution and make the volume to 400 c.c. by the addition of industrial methylated spirit. 45 c.c. of the strong soap solution thus obtained are diluted with methylated spirit (2 vols.) and water (1 vol.) to a litre, allowed to stand for about 24 hours, filtered through a double Swedish filter and standardized against standard calcium chloride solution. The solution will be found a little too strong, and is diluted as before to exact strength, which is attained when 14·25 c.c. are required to form a permanent lather with 50 c.c. of the standard calcium chloride solution. The process is carried out exactly as in determining the hardness of a water. (When diluting the soap solution to exact strength, add the requisite amount of methylated spirit and water mixed—not separately.)

F. Reagents required for the determination of Oxygen absorbed.

Standard solution of potassium permanganate. Dissolve 0·395 gm. of pure potassium permanganate in 1000 c.c. of water. Each c.c. contains 0·0001 gm. of available oxygen.

Potassium iodide solution.—One part of the pure salt dissolved in ten parts of distilled water.

Dilute sulphuric acid.—One part by volume of pure sulphuric acid is mixed with three parts by volume of distilled water, and solution of potassium permanganate dropped in until the whole retains a *very faint* pink tint, after warming to 80° F. for four hours.

Sodium thiosulphate.—One gram of the pure crystallized salt dissolved in 1000 c.c. of water.

Starch indicator.—The best form in which to use this is the solution described on page 131.

THE ANALYTICAL PROCESSES.

The various determinations usually required in the analysis of samples of water, sewage, and sewage effluents will be dealt with in the following order.

*1. The determination of organic carbon and nitrogen (p. 446).
2. ,, ,, total solid matter (p. 462).
3. ,, ,, Nitrogen as nitrates and nitrites (p. 463).
   (i) by Crum's method (p. 463).
   (ii) by Schulze's method (p. 465).
   (iii) by the Copper-zinc couple (p. 466).
   (iv) by Sprengel's method (p. 468).
4. ,, ,, Nitrogen as nitrite (p. 470).
   (i) by Griess's method (p. 470).
   (ii) by Griess-Ilosvay method (p. 470).
5. ,, ,, Suspended matter (p. 471).
6. ,, ,, Combined chlorine (p. 472).

* Seldom used at the present time.

NOTE.—All tables required in water analysis will be found at the end of the book.

1. Collection of Samples.—The points to be considered under this head are, the vessel to be used, the quantity of water required, and the method of ensuring a truly representative sample.

Stoneware bottles should be avoided, as they are apt to affect the hardness of the water, and are more difficult to clean than glass. Stoppered glass bottles should be used it possible; those known as "Winchester Quarts," which hold about two and a half litres each, are very convenient and easy to procure. One of these will contain sufficient for the general analysis of sewage and largely polluted rivers, two for well waters and ordinary rivers and streams, and three for lakes and mountain springs. If a more detailed analysis is required, of course a larger quantity must be taken.

If corks must be used, they should be *new*, and well washed with the water at the time of collection.

In collecting from a well, river, or tank, plunge the bottle itself, if possible, below the surface; but if an intermediate vessel must be used, see that it is thoroughly clean and well rinsed with the water. Avoid the surface water and also any deposit at the bottom.

If the sample is taken from a pump or tap, take care to let the water which has been standing in the pump or pipe run off before collecting, then allow the stream to flow directly into the bottle. If it is to represent a town water-supply, take it from the service pipe communicating directly with the street main, and not from a cistern.

In every case, first fill the bottle *completely* with the water, thus

expelling all gases and vapours, empty it again, rinse once or twice carefully with water, and then fill it nearly to the stopper, and tie down tightly.

At the time of collection note the source of the sample, whether from a deep or shallow well, a river or spring, and also its local name, so that it may be clearly identified.

If it is from a well, ascertain the nature of the soil, subsoil, and water-bearing stratum; the depth and diameter of the well, its distance from neighbouring cesspools, drains, or other sources of pollution; whether it passes through an impervious stratum before entering the water-bearing stratum, and if so, whether the sides of the well above this are, or are not, water-tight.

If the sample is from a river, ascertain the distance from the source to the point of collection; whether any pollution takes place above that point, and the geological nature of the district through which it flows.

If it is from a spring, take note of the stratum from which it issues.

2. Preliminary Observations.—In order to ensure uniformity, the bottle should invariably be well shaken before taking out a portion of the sample for any purpose. The *colour* should be observed through a two-foot tube with plate glass ends half-filled with the sample, placed in a horizontal position, and a well-illuminated white surface observed through it. It is well to compare it with distilled water in a similar vessel. The *taste and odour* are most easily detected when the water is heated to 30°-35° C.

Before commencing the quantitative analysis it is necessary to decide whether the water shall be filtered or not before analysis. This must depend on the purpose for which the examination is undertaken. As a general rule, if the suspended matter is to be determined, the water should be filtered before the determination of organic carbon and nitrogen, nitrogen as ammonia, and total solid residue; if otherwise, it should merely be shaken up. If the suspended matter is *not* determined, the appearance of the water, as to whether it is clear or turbid, should be noted. This is conveniently done when measuring out the quantity to be used for the determination of carbon and nitrogen. If the measuring flask be held between the eye and a good source of light, but with an opaque object such as a window bar, in the line drawn from the eye through the centre of the flask, any suspended particles will be seen well illuminated on a dark ground.

Water derived from a newly sunk well, or one which has been rendered turbid by the introduction of innocuous mineral matter from some temporary and exceptional cause, should be filtered, but the suspended matter in such cases need not usually be determined. The introduction of organic matter of any kind would almost always render the sample useless.

3. Determination of Organic Carbon and Nitrogen.—This should be commenced as soon as the nitrogen as ammonia has been deter-

mined. If that is less than 0·05 part per 100,000, a litre should be used; if more than 0·05, and less than 0·2, half a litre; if more than 0·2, and less than 1·0, a quarter of a litre; if more than 1·0, a hundred c.c., or less. These quantities are given as a guide in dealing with ordinary waters and sewage, but subject to variation in exceptional cases. A quantity which is too large should be avoided as entailing needless trouble in evaporation, and an inconveniently bulky residue and resulting gas. If it is to be filtered before analysis, the same precaution as to filter paper must be taken as for the determination of nitrogen as ammonia, the same filter being generally used.

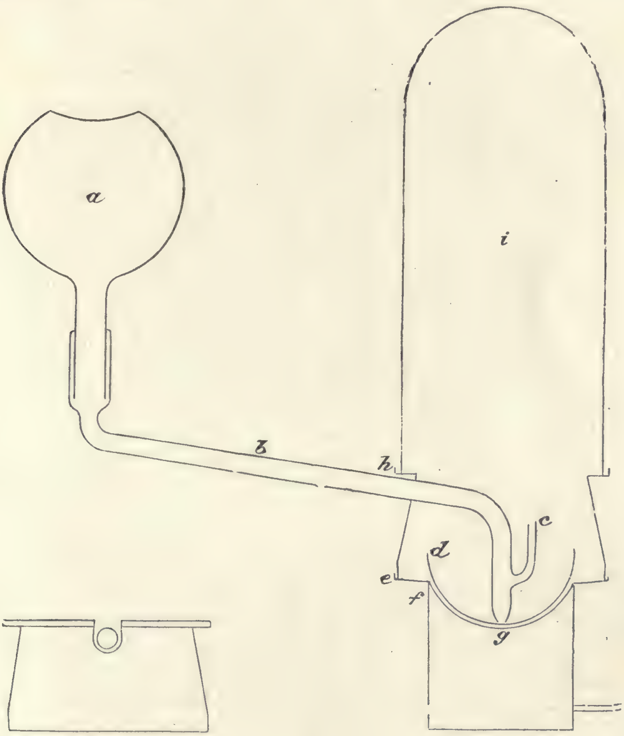


Fig. 61. Fig. 62.

Having measured the quantity to be used, add to it in a capacious flask 15 c.c. of the solution of sulphurous acid (**B.** ii), and boil briskly for a few seconds, in order to decompose the carbonates present. Evaporate to dryness in a hemispherical glass dish, about a decimetre in diameter, and preferably without a lip, supported in a copper dish with a flange (fig. 61 *d e*). The flange has a diameter of about 14 centimetres, is sloped slightly towards the centre, and has a rim of about 5 mm. turned up on its edge, except at one point,

where a small lip is provided. The concave portion is made to fit the contour of the outside of the glass dishes, and is of such a depth as to allow the edge of the dish to rise about 15 mm. above the flange. The diameter of the concavity at *f* is about 90 mm., and the depth at *g* about 30 mm. A thin glass shade, such as is used to protect statuettes, about 30 centimetres high, stands on the flange of the copper dish, its diameter being such as to fit without difficulty on the flange, and leave a sufficient space between its interior surface and the edge of the glass dish. The copper dish is supported on a steam or water bath, and the water as it evaporates is condensed on the interior of the glass shade, runs down into the copper dish, filling the space between it and the glass dish, and then passes off by the lip at the edge of the flange, a piece of tape held by the edge of the glass shade, and hanging over the lip, guiding it into a vessel placed to receive it.

We are indebted to Bischof for an improved apparatus for evaporation, which by keeping the dish always full by a self-acting contrivance permits the operation to proceed without attention during the night, and thus greatly reduces the time required. This form of apparatus is shown in fig. 62. The glass dish *d* is supported by a copper dish *e*, as described above, and resting on the latter is a stout copper ring *h*, which is slightly conical, being 115 mm. in diameter at the top and 130 at the bottom. At the top is a narrow flange of about 10 mm. with a vertical rim of about 5 mm. The diameter across this flange is the same as the diameter of the dish *e*, so that the glass shade *i* will fit securely either on *h* or *e*. The height of the conical ring is about 80 mm.

The automatic supply is accomplished on the well-known principle of the bird fountain, by means of a delivery tube *b*, the upper end of which is enlarged to receive the neck of the flask *a* containing the water to be evaporated, the joint being carefully ground so as to be water-tight. The upper vertical part of *b*, including this enlargement, is about 80 mm. in length, and the sloping part about 260 mm., with a diameter of 13 mm. The lower end which goes into the dish is again vertical for about 85 mm. and carries a side tube *c* of about 3 mm. internal diameter, by which air enters the delivery tube whenever the level of the water in the dish falls below the point at which the side tube joins the delivery tube. The distance from this point to the end of the tube which rests on the bottom of the dish at *g*, and is there somewhat contracted, is about 30 mm. The side tube *c* should not be attached on the side next the flask, as if so the inclined part of *b* passes over its mouth and renders it very difficult to clean. Mills prevents circulation of liquid in the sloping part of the tube by bending it into a slightly undulating form, so that permanent bubbles of air are caught and detained at two points in it. The flask *a* should hold about 1200 c.c., and have a rather narrow neck—about 20 mm.—and a flat bottom. A small slot is cut in the upper edge of the copper ring *h* to accommodate the delivery tube, as shown in fig. 60. Its size and

shape should be such that the tube does not touch the edge of the glass shade *i*, lest water running down the inner surface of the shade should find its way down the outside of the delivery tube into the dish. This being avoided, the opening should be as closely adjusted to the size of the delivery tube as can be. The copper dish *e* should rest on a steam or water bath, so that only the spherical part is exposed to the heat.

After the addition of the 15 c.c. of sulphuric acid, the water may either be boiled in the flask *a*, or in another more capacious one, and then transferred to *a*. It should be allowed to cool before the delivery tube is adjusted, otherwise the joint between the two is liable to become loose by expansion of the cold socket of the delivery tube, after being placed over the hot neck of the flask.

The glass dish having been placed on the copper dish *e*, the conical ring *h* is fitted on, and the flask with the delivery tube attached inverted, as shown in fig. 61, *a b*. This should not be done too hurriedly, and with a little care there is no risk of loss. The flask is supported either by a large wooden filtering stand, the ring of which has had a slot cut in it to allow the neck of the flask to pass or by a clamp applied to the upper end of the delivery tube where the neck of the flask fits in. The delivery tube having been placed in the slot made to receive it, the glass shade is fitted on, and the evaporation allowed to proceed. When all the water has passed from the flask into the dish, the flask and delivery tube and the conical ring *h* may be removed, and the glass placed directly on the dish *e* until the evaporation is complete. If the water is expected to contain a large quantity of nitrates, two or three drops of ferrous chloride (**B.** iv) should be added to the first dishful; and if it contains little or no carbonate, one or two c.c. of hydrogen sodium sulphite (**B.** iii). The former facilitates the destruction of nitrates and nitrites, and the latter furnishes base for the sulphuric acid produced by oxidation of the sulphurous acid, and which would, if free, decompose the organic matter when concentrated by evaporation. An estimate of the quantity of carbonate present, sufficiently accurate for this purpose, may generally be made by observing the quantity of precipitate thrown down on addition of sodium carbonate in the determination of nitrogen as ammonia.

With sewages and very impure waters (containing upwards of 0·1 part of nitrogen as ammonia per 100,000 for example) such great precaution is hardly necessary, and the quantity to evaporate being small, the evaporation may be conducted in a glass dish placed directly over a steam bath, and covered with a drum or disc of filter paper made by stretching the paper by means of two hoops of light split cane, one thrust into the other, the paper being between them, in the way often employed in making dialyzers. This protects the contents of the dish from dust, and also to a great extent, from ammonia which may be in the atmosphere, and which would impair the accuracy of the results. As a glass dish would be in some danger of breaking by the introduction of cold water, the flask containing

the water being evaporated in this or in the first described manner, must be kept on a hot plate or sand bath at a temperature of about 60° or 70° C., and should be covered with a watch-glass. This precaution is not necessary when Bischof's apparatus is used. If, at any time, the water in the flask ceases to smell strongly of sulphurous acid, more should be added. The preliminary boiling may be omitted when less than 250 c.c. is used. When the nitrogen as nitrates and nitrites exceeds 0·5 part, the dish, after the evaporation has been carried to dryness, should be filled with distilled water containing ten per cent. of saturated sulphurous acid solution, and the evaporation again carried to dryness. If it exceeds 1·0 part, a quarter of a litre of this solution should be evaporated on the residue ; if 2·0 parts, half a litre ; and if 5 parts, a litre If less than a litre has been evaporated, a proportionally smaller volume of this solution may be used. The determination of nitrogen as nitrates and nitrites will usually be accomplished before this stage of the evaporation is reached.

M. W. Williams* proposes to avoid the use of sulphurous acid, with its acknowledged disadvantages and defects, by removing the nitric and nitrous acids with the zinc-copper couple and converting them into ammonia. If the amount is large, it is best distilled from a retort into weak acid ; if small, into an empty Nessler tube. The amount so found is calculated into nitrogen as nitrates and nitrites, if the latter are found in the water. The residue, when free from ammonia, is further concentrated, the separated carbonates re-dissolved in phosphoric or sulphurous acid, in just sufficient quantity, then transferred to a glass basin for evaporation to dryness as usual ready for combustion.

In the case of sewage, however, it is advisable to employ hydrogen metaphosphate in the place of sulphurous acid, as the ammonium phosphate is even less volatile than the sulphite. This can only be employed for sewage and similar liquids which are free from nitrates and nitrites. To the measured quantity of liquid to be evaporated add, in the glass dish, 10 c.c. of the hydric metaphosphate (**B.** xii), and, in order to render the residue more convenient to detach from the dish, about half a grain of calcium phosphate (**B.** xiii), and proceed as usual. No ferrous chloride, sulphurous acid, or sodium sulphite is required ; nor is it necessary to boil before commencing the evaporation.

The next operation is the combustion of the residue. The combustion tube should be of hard, difficultly fusible glass, with an internal diameter of about 10 mm. Cut it in lengths of about 430 mm., and heat one end of each in the blowpipe flame to round the edge. Wash well with water, brushing the interior carefully with a tube brush introduced at the end whose edge has been rounded, rinse with distilled water, and dry in an oven. When dry, draw off and close, at the blowpipe, the end whose edge has been left sharp. The tube is then ready for use.

* *J. C. S.* 1881, 144.

Pour on to the perfectly dry residue in the glass dish, standing on a sheet of white glazed paper, a little of the fine cupric oxide (**B.** v), and with the aid of a small elastic steel spatula (about 100 mm. long and 15 mm. wide) carefully detach the residue from the glass and rub it down with the cupric oxide. The spatula readily accom-

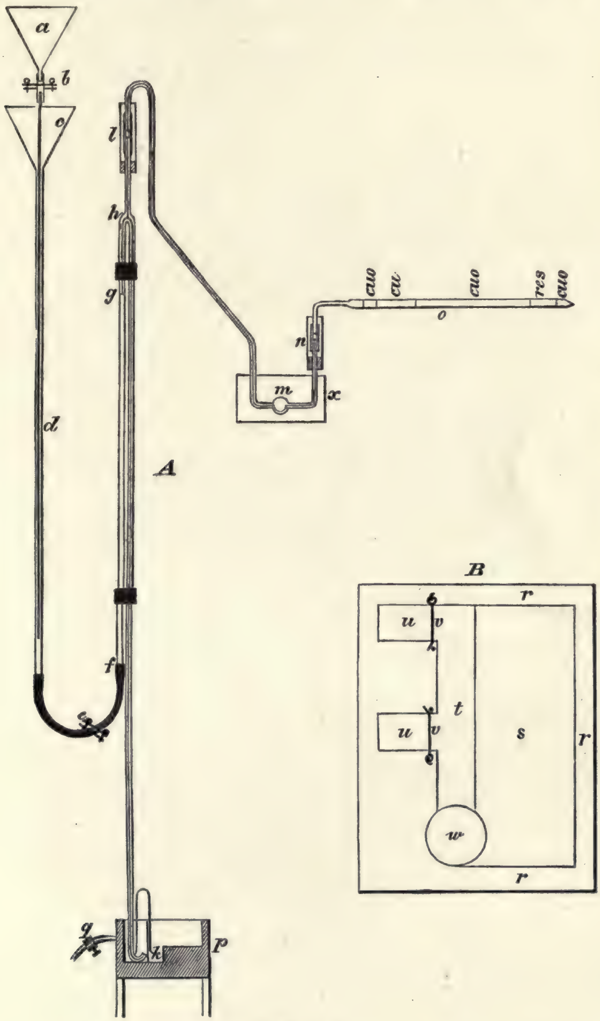


Fig. 63.

modates itself to the curvature of the dish, and effectually scrapes its surface. When the contents of the dish are fairly mixed, fill about 30 mm. of the length of the combustion tube with granulated cupric oxide (**B.** v), and transfer the mixture in the dish to the

tube. This is done in the usual way by a scooping motion of the end of the tube in the dish, the last portions being transferred by the help of a bent card or a piece of clean and smooth platinum foil. Rinse the dish twice with a little fine cupric oxide, rubbing it well round each time with the spatula, and transfer to the tube as before. Any particles scattered on the paper are also to be put in. Fill up to a distance of 270 mm. from the closed end with granular cupric oxide, put in a cylinder of metallic copper (**B.** vi), and then again 20 mm. of granular cupric oxide. This last is to oxidize any traces of carbonic oxide which might be formed from carbonic anhydride by the reducing action of iron or other impurity in the metallic copper. Now draw out the end of the tube so as to form a neck about 100 mm. long and 4 mm. in diameter, fuse the end of this to avoid injury to the india-rubber connector, and bend it at right-angles. It is now ready to be placed in the combustion furnace and attached to the Sprengel pump.

The most convenient form of this instrument for the purpose is shown in fig. 63. The glass funnel *a* is kept supplied with mercury, and is connected by a caoutchouc joint with a long narrow glass tube which passes down nearly to the bottom of a wider tube *d*, 900 mm. long and 10 mm. in internal diameter. The upper end of *d* is cemented into the throat of a glass funnel *c* from which the neck has been removed. A screw clamp *b* regulates the flow of mercury down the narrow tube. A piece of ordinary glass tube *f g*, about 6 mm. in diameter and 600 mm. in length, is attached to *g* to a tube *g h k*, about 6 mm. in diameter, 1500 mm. long, with a bore of 1 mm. This is bent sharply on itself at *h*, the part *h k* being 1300 mm. long, and the two limbs are firmly lashed together with copper wire at two points, the tubes being preserved from injury by short sheaths of caoutchouc tube. The end *k* is recurved for the delivery of gas. At the top of the bend at *h*, a piece of ordinary tube *h l*, about 120 mm. long and 5 mm. in diameter, is sealed on. The whole *l k* is kept in a vertical position by a loose support or guide, near its upper part, the whole of its weight resting on the end *k*, so that it is comparatively free to move. It is connected at *f* with the lower end of *d*, by means of a piece of caoutchouc tube covered with tape, and furnished with a screw clamp *e*. At *l* it is connected with the combustion tube *o*, by the connecting tube *l m n*, which is made of tube similar to that used for *h k*. A cork slides on *h l*, which is fitted into the lower end of a short piece of tube of a width sufficient to pass easily over the caoutchouc joint connecting the tubes at *l*. After the joint has been arranged (the ends of the tubes just touching) and bound with wire, the cork and wide tube are pushed over it and filled with glycerine. The joint at *n* is of exactly the same kind, but as it has to be frequently disconnected, water is used instead of glycerine, and the caoutchouc is not bound on to the combustion tube with wire. It will be seen that the joint at *l* is introduced chiefly to give flexibility to the apparatus. At *m* is a small bulb blown on the tube for the purpose of receiving water produced in

the combustion. This is immersed in a small water trough *x*. The tube *h k* stands in a mercury trough *p*, which is shown in plan on a larger scale at B.

This trough should be cut of a solid piece of mahogany, as it is extremely difficult to make joints to resist the pressure of such a depth of mercury. It is 200 mm. long, 155 mm. wide, and 100 mm. deep, outside measurement. The edge *r r* is 13 mm. wide, and the shelf *s* 65 mm. wide, 174 mm. long, and 50 mm. deep from the top of the trough. The channel *t* is 25 mm. wide and 75 mm. deep, having at one end a circular well *w*, 42 mm. in diameter, and 90 mm. deep. The recesses *u u* are to receive the ends of two Sprengel pumps. They are each 40 mm. long, 25 mm. wide, and of the same depth as the channel *t*. A short iron wire *c*, turning on a small staple, and resting at the other end against an iron pin, stretches across each of these, and serves as a kind of gate to support the test tube, in which the gas delivered by the pump is collected. The trough stands upon four legs, 75 mm. high, and is provided at the side with a tube and screw clamp *q*, by which the mercury may be drawn off to the level of the shelf *s*.

The combustion tube being placed in the furnace, protected from the direct action of the flame by a sheet-iron trough lined with asbestos, and the water joint at *n* adjusted, the gas is lighted at the front part of furnace so as to heat the whole of the metallic copper and part of the cupric oxide. A small screen of sheet iron is adjusted astride the combustion tube to protect the part beyond the point up to which the gas is burning from the heat.

At the same time a stream of mercury is allowed to flow from the funnel *a*, which fills the tubes *d* and *f* until it reaches *h*, when it falls in a series of pellets down the narrow tube *h k*, each carrying before it a quantity of air drawn from the combustion tube. The flow of mercury must be controlled by means of the clamps *b* and *e*, so as not to be too rapid to admit of the formation of these separate pistons, and especially, care should be taken not to permit it to go so fast as to mount into the connecting tube *l m n*, as it cannot be removed thence except by disconnecting the tube. During the exhaustion, the trough *x* is filled with hot water to expel from the bulb *m* any water condensed from a previous operation. In about ten minutes the mercury will fall in the tube *h k* with a loud, sharp, clicking sound, showing that the vacuum is complete. As soon as this occurs, the pump may be stopped, a test tube filled with mercury inverted over the delivery end of the tube *k*, cold water substituted for hot in the trough *x*, the iron screen removed, and combustion proceeded with in the usual way. This will take from fifty to sixty minutes. As soon as the whole of the tube is heated to redness, the gas is turned off, and the tube immediately exhausted, the gases produced being transferred to the tube placed to receive them. When the exhaustion is complete, the test tube of gas may be removed in a small beaker, and transferred to the gas analysis apparatus.

The gas collected consists of carbonic anhydride, nitric oxide, nitrogen, and (very rarely) carbonic oxide, which can readily be separated and determined by the ordinary methods of gas analysis. This is rapidly accomplished with the apparatus, shown in the

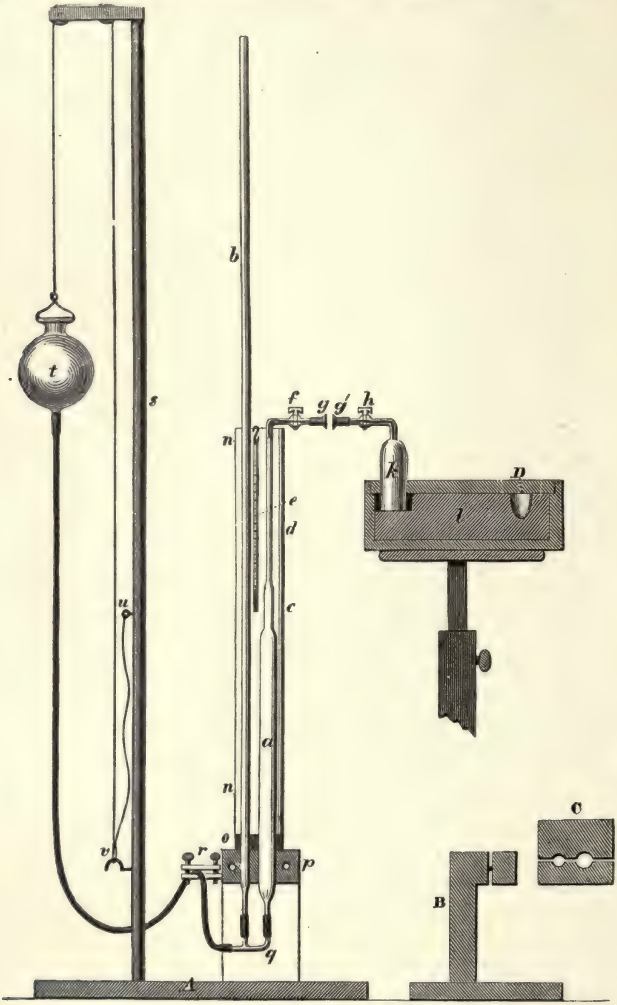


Fig. 64.

accompanying diagram, Fig. 64, which, whilst it does not permit of analysis by explosion, leaves nothing to be desired for this particular operation. It is essentially that described by Frankland*, but is slightly modified in arrangement. In the diagram, *a c d* is a measuring tube, of which the cylindrical portion *a* is 370 mm. long,

* *J. C. S.* [2] vi. 109.

and 18 mm. in internal diameter, the part *c* 40 mm. long and 7 mm. in diameter, and the part *d* 175 mm. long and 2·5 mm. in diameter. To the upper end of *d* a tube, with a capillary bore and stop-cock *f*, is attached, and bent at right-angles. Allowing 20 mm. for each of the conical portions at the joints between *a* and *c*, and *c* and *d*, and 25 mm. for the vertical part of the capillary tube, the vertical measurement of the entire tube is 650 mm. It is graduated carefully from below upward, at intervals of 10 mm., the zero being 100 mm. from the end, as about that length of it is hidden by its support, and therefore unavailable. The topmost 10 mm. of *d* should be divided into single millimetres. At the free end of the capillary tube a small steel cap, shown in fig. 65, B, is cemented gas tight. The lower end of *a* is drawn out to a diameter of 5 mm.

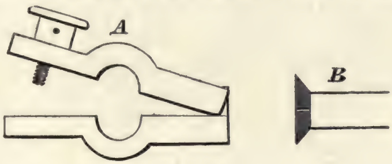


Fig. 65.

The tube *b* is about 1·2 metre long, and 6 mm. internal diameter, is drawn out like *a* at the lower end, and graduated in millimetres from below upward, the zero being about 100 mm. from the end.* The tubes *a c d* and *b* pass through a caoutchouc stopper *o*, which fits into the lower end of a glass cylinder *n n*, intended to contain water to give a definite temperature to the gas in measuring. The zeros of the graduations should be about 10 mm. above this stopper. Immediately below this the tubes are firmly clasped by the wooden clamp *p* (shown in end elevation and plan at fig. 64, B, C), the two parts of which are drawn together by screws, the tubes being protected from injury by a piece of caoutchouc tube fitted over each. The clamp is supported on an upright piece of wood, screwed firmly to the base A. It the stopper *o* is carefully fitted, and the tubes tightly clamped, no other support than *p* will be necessary. The tubes below the clamp are connected by joints of caoutchouc covered with tape, and strongly bound with wire, to the vertical legs of the union piece *q*, to the horizontal leg of which is attached a long caoutchouc tube of about 2 mm. internal diameter, which passes to the glass reservoir *t*. This tube must be covered with strong tape, or (less conveniently) have a lining of canvas between two layers of caoutchouc, as it will be exposed to considerable pressure. In its course it passes through the double screw steel pinch-cock *r*, the lower bar of which is fixed to the side of the clamp *p*. It is essential that the screws of the pinch-cock should have smooth collars like that shown in fig. 65 A, and that the upper surface of the upper bar of the pinch-cock should be quite flat, the surfaces between which the tube is passed being cylindrical.

* The graduation is not shown in the diagram.

Frankland has introduced a form of joint by which the steel caps and clamp are dispensed with. The capillary tube at the upper end of *a c d* is expanded into a small cup or funnel, and the capillary tube of the laboratory vessel bent *twice* at right-angles, the end being drawn out in a conical form to fit into the neck of the above-named cup. The opposed surfaces are fitted by grinding or by covering the conical end of the laboratory vessel with thin sheet caoutchouc. The joint is kept tight by an elastic band attached at one end to the stand, and at the other to a hook on the horizontal tube of the laboratory vessel, and the cup is filled with mercury.

In the base A is fixed a stout iron rod, 1·4 metre long, with a short horizontal arm at its upper end, containing two grooved pulleys. The reservoir *t* is suspended by a cord passing over these pulleys, and attached to an eye *u* in the iron rod, the length of the cord being such that, when at full stretch, the bottom of the reservoir is level with the bottom of the clamp *p*. A loop is made on the cord, which can be secured by a hook *v* on the rod, so that when thus suspended, the bottom of *t* is about 100 mm. above the stop-cock *f*. A stout elastic band fitted round *t* at its largest diameter acts usefully as a fender to protect it from an accidental blow against the iron rod. A thermometer *e*, suspended by a wire hook from the edge of the cylinder, *n n*, gives the temperature of the contained water, the uniformity of which may be ensured (though it is scarcely necessary) by passing a slow succession of bubbles of air through it or by moving up and down in it a wire with its end bent into the form of a ring. The jar *k* is called the *laboratory vessel*, and is 100 mm. high, and 38 mm. in internal diameter, having a capillary tube, glass stop-cock, and steel cap *g h* exactly like *f g*. The mercury trough *l* is shown in figs. 66 and 67. It is of solid mahogany, 265 mm. long, 80 mm. broad, and 90 mm. deep, outside measurement. The rim *a a a a* is 8 mm. broad and 15 mm. deep. The excavation *b* is 230 mm. long, 26 mm. broad, and 65 mm. deep, with a circular cavity to receive the laboratory vessel sunk at one end, 45 mm. in diameter, and 20 mm. in depth below the top of the excavation. Two small lateral indentations *c c* (fig. 67) near the other end

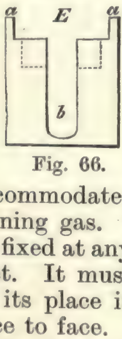


Fig. 66.

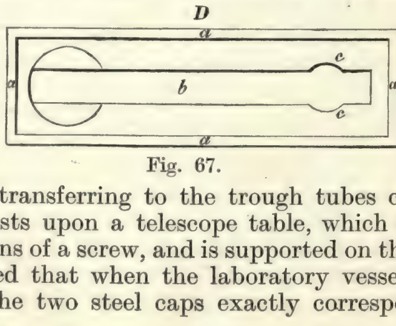


Fig. 67.

accommodate a capsule for transferring to the trough tubes containing gas. This trough rests upon a telescope table, which can be fixed at any height by means of a screw, and is supported on three feet. It must be so arranged that when the laboratory vessel is in its place in the trough the two steel caps exactly correspond face to face.

The difference of level of the mercury in the tubes *b* and *a c d*,

caused by capillary action, when both are freely open to the air, must be ascertained by taking several careful observations. This will be different for each of the portions *a c* and *d*, and must be added to or deducted from the observed pressure, as the mercury when thus freely exposed in both tubes to the atmospheric pressure stands in *a c* or *d* above or below that in *b*. This correction will include also any that may be necessary for difference of level of the zeros of the graduations of the two tubes, and, if the relative positions of these be altered, it must be redetermined. A small telescope, sliding on a vertical rod, should be used in these and all other readings of the level of mercury.

The capacity of the measuring tube *a c d* at each graduation must now be determined. This is readily done by first filling the whole apparatus with mercury, so that it drips from the cap *g*. The stop-cock *f* is then closed, a piece of caoutchouc tube slipped over the cap, and attached to a funnel supplied with distilled water. The reservoir *t* being lowered, the clamp *r* and the stop-cock *f* are opened, so that the mercury returns to the reservoir, water entering through the capillary tube. As soon as it is below the zero of the graduation, the stop-cock *f* is closed, the funnel and caoutchouc tube removed from the cap, and the face of the last slightly greased in order that water may pass over it without adhering. Now raise the reservoir, open the stop-cock *f*, and allow the water to flow gently out until the top of the convex surface of the mercury in *a* just coincides with the zero of the graduation. The mercury should be so controlled by the clamp *r* that the water issues under very slight pressure. Note the temperature of the water in the water-jacket, and proceed with the expulsion of the water, collecting it as it drops from the steel cap, in a small carefully weighed glass flask. When the mercury has risen through 100 mm. stop the flow of water, and weigh the flask. The weight of water which was contained between the graduations 0 and 100 on the tube is then known, and if the temperature be 4° C., the weight in grams will express the capacity of that part of the tube in cubic centimetres. If the temperature be other than 4° C., the volume must be calculated by the aid of the co-efficient of expansion of water by heat. In a similar way the capacity of the tube at successive graduations about 100 mm. apart is ascertained, the last determination in *a* being at the highest, and the first in *c* at the lowest graduation on the cylindrical part of each tube; the tube between these points and similar points on *c* and *d* being so distorted by the glass blower that observations could not well be made. The capacity at a sufficient number of points being ascertained, that at each of the intermediate graduations may be calculated, and a table arranged with the capacity marked against each graduation. As the calculations in the analysis are made by the aid of logarithms, it is convenient to enter on this table the logarithms of the capacities instead of the natural numbers.

In using the apparatus, the stop-cocks on the measuring tube and laboratory vessel should be slightly greased with a mixture of resin

cerate and oil, or vaseline, the whole apparatus carefully filled with mercury, and the stop-cock *f* closed ; next place the laboratory vessel in position in the mercury trough, and suck out the air. This is readily and rapidly done by the aid of a short piece of caoutchouc tube, placed in the vessel just before it is put into the mercury trough, and drawn away as soon as the air is removed. Suck out any small bubbles of air left still through the capillary tube, and as soon as the vessel is entirely free from air close the stop-cock. Slightly grease the face of both caps with resin cerate (to which a little oil should be added if very stiff), and clamp them tightly together. On opening both stop-cocks mercury should flow freely through the capillary communication thus formed, and the whole should be quite free from air. To ascertain if the joints are all in good order, close the stop-cock *h*, and lower the reservoir *t* to its lowest position ; the joints and stop-cocks will thus be subjected to a pressure of nearly half an atmosphere, and any leakage would speedily be detected. If all be right, restore the reservoir to its upper position.

Transfer the tube containing the gas to be analyzed to an ordinary porcelain mercury trough ; exchange the beaker in which it has been standing for a small porcelain capsule, and transfer it to the mercury trough *l*, the capsule finding ample room where the trough is widened by the recess D.

Carefully decant the gas to the laboratory vessel, and add a drop or two of potassium dichromate solution (**B.** vii) from a small pipette with a bent capillary delivery tube, to ascertain if the gas contains any sulphurous anhydride. If so, the yellow solution will immediately become green from the formation of a chromic salt, and the gas must be allowed to stand over the chromate for four or five minutes, a little more of the solution being added it necessary. The absorption may be greatly accelerated by gently shaking from time to time the stand on which the mercury trough rests, so as to cause the solution to wet the sides of the vessel. With care this may be done without danger to the apparatus. Mercury should be allowed to pass slowly into the laboratory vessel during the whole time, as the drops falling tend to maintain a circulation both in the gas and in the absorbing liquid. The absence of sulphurous anhydride being ascertained, both stop-cocks are set fully open, the reservoir *t* lowered, and the gas transferred to the measuring tube. The stop-cock *h* should be closed as soon as the liquid from the laboratory vessel is within about 10 mm. of it. The bore of the capillary tube is so fine, that the quantity of gas contained in it is too small to affect the result. Next bring the top of the meniscus of mercury seen through the telescope exactly to coincide with one of the graduations on the measuring tube, the passage of mercury to or from the reservoir being readily controlled by the pinch-cock *r*. Note the position of the mercury in the measuring tube and in the pressure tube *b*, the temperature of the water-jacket, and the height of the barometer, the level of the mercury in the pressure

tube and barometer being read to the tenth of a mm. and the thermometer to 0·1° C. This done, introduce into the laboratory vessel from a pipette with a bent point, a few drops of potassium hydrate solution (**B.** viii), and return the gas to the laboratory vessel. The absorption of carbonic anhydride will be complete in about three to five minutes, and if the volume of the gas is large, may be much accelerated by gently shaking the stand from time to time, so as to throw up the liquid on the sides of the vessel. If the small pipettes used to introduce the various solutions are removed from the mercury trough gently, they will always contain a little mercury in the bend, which will suffice to keep the solution from flowing out, and they may be kept in readiness for use standing upright in glass cylinders or other convenient supports. At the end of five minutes the gas, which now consists of nitrogen and nitric oxide, is again transferred to the measuring tube, and the operation of measuring repeated; the barometer, however, need not be observed, under ordinary circumstances, more than once for each analysis, as the atmospheric pressure will not materially vary during the twenty-five to thirty minutes required. Next pass into the laboratory vessel a few drops of saturated solution of pyrogallic acid (**B.** ix), and return the gas upon it. The object of adding the pyrogallic acid at this stage is to ascertain if oxygen is present, as sometimes happens when the total quantity of gas is very small, and the vacuum during the combustion but slightly impaired. Under such circumstances, traces of oxygen are given off by the cupric oxide, and pass so rapidly over the metallic copper as to escape absorption. This necessarily involves the loss of any nitric oxide which also escapes the copper, but this is such a very small proportion of an already small quantity that its loss will not appreciably affect the result. If oxygen be present, allow the gas to remain exposed to the action of the pyrogallate until the liquid when thrown up the sides of the laboratory vessel runs off without leaving a dark red stain. If oxygen be not present, a few bubbles of that gas (**B.** xi) are introduced to oxidize the nitric oxide to nitrogen peroxide, which is absorbed by the potassium hydrate. The oxygen may be very conveniently added from the gas pipette shown in fig. 68, where *a b* are glass bulbs of about 50 mm. diameter, connected by a glass tube, the bore of which is constricted at *c*, so as to allow mercury to pass but slowly from one bulb to the other, and thus control the passage of gas through the narrow delivery tube *d*. The other end *e* is provided with a short piece of caoutchouc tube, by blowing through which any desired quantity of gas may be readily delivered. Care must be taken after use that the delivery tube is not removed from the trough till the angle *d* is filled with mercury.

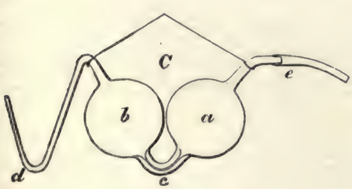


Fig. 68.

To replenish the pipette with oxygen, fill the bulb *b* and the tubes *c* and *d* with mercury ; introduce the point of *d* into a tube of oxygen standing in the mercury trough, and draw air from the tube *e*. The gas in *b* is confined between the mercury in *c* and that in *d*.

When the excess of oxygen has been absorbed as above described, the residual gas, which consists of nitrogen, is measured, and the analysis is complete.*

There are thus obtained three sets of observations, from which, by the usual methods, we may calculate A the total volume, B the volume of nitric oxide and nitrogen, and C the volume of nitrogen, all reduced to 0° C. and 760 mm. pressure ; from these may be obtained—

$$A-B=\text{vol. of } CO_2,$$

$$\frac{B-C}{2}+C=\frac{B+C}{2}=\text{vol. of N},$$

and hence the weight of carbon and nitrogen can be readily found.

It is much less trouble, however, to assume that the gas in all three stages consists wholly of nitrogen ; then, if A be the weight of the total gas, B its weight after treatment with potassium hydrate, and C after treatment with pyrogallate, the weight of carbon will be $(A-B)\frac{3}{7}$ and the weight of nitrogen $\frac{B+C}{2}$; for the weights of carbon and nitrogen in equal volumes of carbon anhydride and nitrogen, at the same temperature and pressure, are as 6 : 14 ; and the weights of nitrogen in equal volumes of nitrogen and nitric oxide are as 2 : 1.

The weight of 1 c.c. of nitrogen at 0° C. and 760 mm. is 0·0012562† gm., and the formula for the calculation is $w=\frac{0{\cdot}0012562\times v\times p}{(1+0{\cdot}00367t)760}$ in which w = the weight of nitrogen, v the volume, p the pressure corrected for tension of aqueous vapour, and t the temperature in degrees centigrade. To facilitate this calculation, there is given in Table 2 the logarithmic value of the expression $\frac{0{\cdot}0012562}{(1+0{\cdot}00367t)\ 760}$ for each tenth of a degree from 0° to 29·9° C., and in Table 1 (Tables 1 to 8 are inserted at the end of the book) the tension of aqueous vapour in millimetres of mercury. As the measuring tube is always kept moist with water, the gas when measured is always saturated with aqueous vapour.

* When the quantity of carbon is very large indeed, traces of carbonic oxide are occasionally present in the gas, and will remain with the nitrogen after treatment with alkaline pyrogallate. When such excessive quantities of carbon are found, the stop-cock *f* should be closed when the last measurement is made, the laboratory vessel detached, washed, and replaced filled with mercury. Introduce then a little solution of cuprous chloride (**B.** x), and return the gas upon it. Any carbonic oxide will be absorbed, and after about five minutes the remaining nitrogen may be measured. In more than twenty consecutive analyses of waters of very varying kinds, not a trace of carbonic oxide was found in any of the gases obtained on combustion.

†This is Regnault's value. The most recent determinations by Lord Rayleigh and by Gray give the value 0·0012507 gm.

The following example will show the precise mode of calculation :—

	A Total.	B After Absorption of CO^2.	C Nitrogen.
Volume of gas . . .	4·4888 c.c.	0·26227 c.c.	0·26227 c.c.
Temperature	13·5°	13·6°	13·7°
	mm.	mm.	mm.
Height of Mercury in *a, c, d*, .	310·0	480·0	480·0
,, ,, ,, *b*, . .	193·5	343·5	328·2
Difference . . .	116·5	136·5	151·8
Plus tension of aqueous vapour	11·5	11·6	11·7
	128·0		
Deduct correction for capillarity	0·9	Add for capillarity 2·2	2·2
	127·1	150·3	165·7
	769·8	769·8	769·8
Deduct this from height of bar .	127·1	150·3	165·7
Tension of dry gas . . .	642·7	619·5	604·1
Logarithm of volume of gas .	0·65213	$\bar{1}$·41875	$\bar{1}$·41875
,, ,, $\frac{0·0012562}{(1+0·00367t)760}$.	$\bar{6}$·19724	$\bar{6}$·19709	$\bar{6}$·19694
,, ,, tension of dry gas .	2·80801	2·79204	2·78111
Logarithm of weight of gas calculated as N. . . .	$\bar{3}$·65738 =0·0045434	$\bar{4}$·40788 0·0002558	$\bar{4}$·39680 0·0002494 gm.

From these weights, those of carbon and of nitrogen are obtained by the use of the formulæ above mentioned. Thus—

$$\begin{array}{rl} A-B= & 0·0042876 \\ \times & 3 \\ \div 7) & 0·0128628 \\ \text{Weight of carbon,} & 0·001837 \end{array} \qquad \begin{array}{rl} B+C= & 0·0005052 \\ & \div 2 \\ \text{Weight of nitrogen,} & 0·0002526 \end{array}$$

When carbonic oxide is found, the corresponding weight of nitrogen may be found in a similar manner, and should be added to that corresponding to the carbonic anhydride before multiplying by $\frac{3}{7}$, and must be deducted from the weight corresponding to the volume after absorption of carbonic anhydride.

As it is impossible to attain to absolute perfection of manipulation and materials, each analyst should make several blank experiments by evaporating a litre of pure distilled water (**B.** i) with the usual quantities of sulphurous acid and ferrous chloride, and, in addition, 0·1 gm. of freshly ignited sodium chloride (in order to furnish a tangible residue). The residue should be burnt and the resulting gas analyzed in the usual way, and the average amounts of carbon and nitrogen thus obtained deducted from the results of all analyses. This correction, which may be about 0·0001 gm. of C and 0·00005 gm. of N, includes the errors due to the imperfection of the vacuum produced by the Sprengel pump, nitrogen retained in the cupric

oxide, ammonia absorbed from the atmosphere during evaporation, etc.

When the quantity of nitrogen as ammonia exceeds 0·007 part per 100,000, there is a certain amount of loss of nitrogen during the evaporation by dissipation of ammonia. This appears to be very constant, and is given in Table 3, which is calculated from Table 5, which has been kindly furnished by the late Sir E. Frankland. The number in this table corresponding to the quantity of nitrogen as ammonia present in the water analyzed should be added to the amount of nitrogen found by combustion. The number thus obtained includes the nitrogen as ammonia, and this must be deducted to ascertain the *organic* nitrogen. If "ammonia" is determined instead of "nitrogen as ammonia," Table 5 may be used.

When, in operating upon sewage, hydrogen metaphosphate has been employed, Tables 4 or 6 should be used.

4. Determination of Total Solid Matter.—This is done by evaporating a known quantity of the water to dryness in a weighed platinum dish on the water-bath. When the residue is not required for any subsequent determination, 250 c.c. are generally taken; but when, as is often the case, the residue is to be used for the determination of nitric and nitrous nitrogen by Crum's method, the amounts usually taken are as follows:—For water supplies and river water—500 c.c. and shallow well waters—250 c.c.

The sample used should be filtered or unfiltered according to the decision made in that respect at the commencement of the analysis.

For sewage and effluents take 100 c.c.

It is desirable to support the platinum dish during evaporation in a glass ring with a flange, shaped like the top of a beaker, the cylindrical part being about 20 mm. deep. This is dropped into the metal ring on the water-bath, and thus lines the metal with glass, and keeps the dish clean. A glass disc with a hole in it to receive the dish is not satisfactory, as drops of water conveying solid matter find their way across the under surface from the metal vessel to the dish, and thus soil it. As soon as the evaporation is complete, the dish with the residue is removed, its outer surface wiped dry with a cloth, and it is dried in a water or steam oven for about three hours. It is then removed to a desiccator, allowed to cool, weighed as rapidly as possible, returned to the oven, and weighed at intervals of an hour, until between two successive weighings it has lost less than 0·001 gm.*

* There is some diversity of opinion as to the temperature at which the total solids in water should be dried previous to weighing. The Committee appointed by the Society of Public Analysts (see *Analyst* vi 1881, 137) recommended 220° F. (104·4° C.). Dr. Rideal ("Water and its Purification") recommends 120° C. Prof. Stillman ("Engineering Chemistry") gives 105° C. Dr. Thresh ("Examination of Waters and Water Supplies") dries at 180° C., "because at this temperature magnesium sulphate retains a definite proportion of water and calcium sulphate loses the whole of its water of crystallization, the results consequently being much more uniform and satisfactory than at a lower temperature." Dr. Fowler ("Sewage Works Analyses") dries the solids from sewages and effluents at 100-110° C. Dr. Mc Gowan (*lec. cit.*) states that the total solids in sewages and effluents should be dried in an air-bath at 110° C. till the weight becomes constant. Hence it is important for analysts to state on water and sewage certificates the temperature at which the solids have been dried.

If the residue is not wanted for any other purpose, the dish should be gradually heated to redness and note made of any changes that may take place, especially smell, scintillation, slight darkening or blackening, and partial fusion. The ignited residue may be tested for the presence of phosphoric acid (see p. 477).

5. Determination of Nitrogen as Nitrates and Nitrites (Crum's method).—The residue obtained in the preceding operation may be used for this determination. Treat it with about 30 c.c. of hot distilled water, taking care to submit the whole of the residue to its action. To ensure this it is advisable to rub the dish gently with the finger, so as to detach the solid matter as far as possible, and facilitate the solution of the soluble matters. The finger may be covered by a caoutchouc finger-stall. Then filter through a very small filter of Swedish paper, washing the dish several times with small quantities of hot distilled water.

Fig. 69.

The filtrate must be evaporated in a very small beaker, over a steam bath, until reduced to about 1 c.c., or even to dryness. This concentrated solution is introduced into the glass tube shown in fig. 69, standing in the porcelain mercury trough, filled up to the stop-cock with mercury. (If the nitrometer of Lunge is used in place of Crum's tube, the use of the laboratory tube and gas apparatus is avoided.) The tube is 210 mm. in total length and 15 mm. in internal diameter. By pouring the liquid into the cup at the top, and then cautiously opening the stop-cock, it may be run into the tube without admitting any air. The beaker is rinsed once with a very little hot distilled water, and then two or three times with strong sulphuric acid (**C.** i), the volume of acid being to that of the aqueous solution about as 3 : 2. The total volume of acid and water should be about 6 c.c. Should any air by chance be admitted at this stage, it may readily be removed by suction, the lips being applied to the cup. With care there is but little danger of getting acid into the mouth.

In a few cases carbonic anhydride is given off on addition of sulphuric acid, and must be sucked out before proceeding.

Now grasp the tube firmly in the hand, closing the open end by the thumb, which should be first moistened; withdraw it from the trough, incline it at an angle of about 45°, the cup pointing from you, and shake it briskly with a rapid motion in the direction of its length, so as to throw the mercury up towards the stop-cock. After a very little practice there is no danger of the acid finding its way down to the thumb, the mixture of acid and mercury being confined to a comparatively small portion of the tube. In a few seconds some of the mercury becomes very finely divided; and if nitrates be present, in about a minute or less nitric oxide is evolved, exerting a strong pressure on the thumb. Mercury is allowed to escape as the reaction proceeds, by partially, but not wholly, relaxing the pressure of the thumb. A slight excess of pressure

should be maintained within the tube to prevent entrance of air during the agitation, which must be continued until no more gas is evolved.

When the quantity of nitrate is very large, the mercury, on shaking, breaks up into irregular masses, which adhere to one another as if alloyed with lead or tin, and the whole forms a stiff dark-coloured paste, which it is sometimes very difficult to shake; but nitric oxide is not evolved for a considerable time, then comes off slowly, and afterwards with very great rapidity. To have room for the gas evolved, the operator should endeavour to shake the tube so as to employ as little as possible of the contained mercury in the reaction. At the close of the operation the finely divided mercury will consist for the most part of minute spheres, the alloyed appearance being entirely gone. An experiment with a large quantity of nitrate may often be saved from loss by firmly resisting the escape of mercury, shaking until it is judged by the appearance of the contents of the tube that the reaction is complete, and then on restoring the tube to the mercury trough, allowing the finely-divided mercury also to escape in part. If the gas evolved be not more than the tube will hold, and there be no odour of nitric peroxide from the escaped finely-divided mercury, the operation may be considered successful. If the amount of nitrate be too large, a smaller quantity of the water must be evaporated and the operation repeated. When no nitrate is present, the mercury usually manifests very little tendency to become divided, that which does so remains bright, and the acid liquid does not become so turbid as in other cases.

The reaction completed, the tube is taken up closed by the thumb, and the gas is decanted into the laboratory vessel, and measured in the usual way in the gas apparatus. The nitric acid tube is of such a length that when the cup is in contact with the end of the mercury trough the open end is just under the centre of the laboratory vessel. If any acid has been expelled from the tube at the close of the shaking operation, the end of the tube and the thumb should be washed with water before introducing into the mercury trough of the gas apparatus, so as to remove any acid which may be adhering, which would destroy the wood of the trough. Before passing the gas into the measuring tube of the gas apparatus, a little mercury should be allowed to run into the laboratory vessel to remove the acid from the entrance to the capillary tube.

As nitric oxide contains half its volume of nitrogen, if half a litre of water has been employed, the volume of nitric oxide obtained will be equal to the volume of *nitrogen* present as nitrates and nitrites in one litre of the water, and the weight of the nitrogen may be calculated as directed in the paragraph on the determination of organic carbon and nitrogen (see p. 460).

When more than 0·08 part of nitrogen as ammonia is present in 100,000 parts of liquid, there is danger of loss of nitrogen by decomposition of ammonium nitrite on evaporation; and therefore

the residue from the determination of total solid matter cannot be used. In such cases acidify a fresh quantity of the liquid with dilute sulphuric acid, add solution of potassium permanganate, a little at a time, until the pink colour remains for about a minute, and render the liquid just alkaline to litmus paper with sodium carbonate. The nitrites present will then be converted into nitrates and may be evaporated without fear of loss. Use as little of each reagent as possible.

Allen* advocated the use of Lunge's nitrometer in place of Crum's tube and, to obviate the difficulty in reading the volume of gas which sometimes arises on account of the mercurial froth, he used two nitrometers side by side. In these he worked, under identical conditions, the water-residue and a standard solution of potassium nitrate respectively. A simple calculation then gives the amount of nitrogen required. Allen stated that it is not necessary to make a test experiment each time, as provided the nitrometer tap is tight, the standard measure of gas obtained from the nitre solution may be kept for an indefinite period. (For list of Nitrogen Conversion Factors, see p. 285).

6. Determination of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, with but little Ammonia or Organic Nitrogen.—When the quantity of soluble matter is excessive, as, for example, in sea-water, the preceding method is inapplicable, as the solution to be employed cannot be reduced to a sufficiently small bulk to go into the shaking tube. If the quantity of organic nitrogen be less than 0·1 part in 100,000 the nitrogen as nitrates and nitrites may generally be determined by the following modification of Schulze's method devised by E. T. Chapman. To 200 c.c. of the water add 10 c.c. of sodium hydrate solution (**C.** v), and boil briskly in an open porcelain dish until it is reduced to about 70 c.c. When cold pour the residue into a tall glass cylinder of about 120 c.c. capacity, and rinse the dish with water free from ammonia. Add a piece of aluminium foil of about 15 sq. centim. area, loading it with a piece of clean glass rod to keep it from floating. Close the mouth of the cylinder with a cork, bearing a small tube filled with pumice (**C.** vi), moistened with hydric chloride free from ammonia (**C.** vii).

Hydrogen will speedily be given off from the surface of the aluminium, and in five or six hours the whole of the nitrogen as nitrates and nitrites will be converted into ammonia. Transfer to a small retort the contents of the cylinder, together with the pumice, washing the whole apparatus with a little water free from ammonia. Distil, and determine the ammonia in the usual way with Nessler solution. It appears impossible wholly to exclude ammonia from the reagents and apparatus, and therefore some blank experiments should be made to ascertain the correction to be applied for this. This correction is very small, and appears to be nearly constant.

* *Analyst*, 1880, 181.

7. Determination of Nitrates as Ammonia by the Copper-zinc Couple.—It is well known that when zinc is immersed in copper sulphate solution it becomes covered with a spongy deposit of precipitated copper. If the solution of copper sulphate be sufficiently dilute, this deposit of copper is black in colour and firmly adherent to the zinc. It is, however, not so generally known that the zinc upon which copper has thus been deposited possesses the power of decomposing pure distilled water at the ordinary temperature, and that it is capable of effecting many other decompositions which zinc alone cannot. Among these is the decomposition of nitrates, and the transformation of the nitric acid into ammonia. Gladstone and Tribe have shown that the action of the "copper-zinc couple" upon a nitre solution consists in the electrolysis of the nitre, resulting in the liberation of hydrogen and the formation of zinc oxide. The nascent hydrogen liberated on the surface of the copper reduces the nitrate to nitrite and this in turn to ammonia. M. W. Williams* has shown that even in very dilute solutions of nitre the nitric acid can be completely converted into ammonia in this manner with considerable rapidity; and further, that the reaction may be greatly hastened by taking advantage of the influence of temperature, acids, and certain neutral salts, which increase the electrolytic action of the couple. His experiments prove that carbonic acid—feeble acid as it is—suffices to treble the speed of the reaction, and that traces of sodium chloride (0·1 per cent.) accelerated it nearly as much as carbonic acid. A rise of a few degrees in temperature was also found to hasten the reaction in a very marked degree. The presence of alkalies, alkaline earths, and salts having an alkaline reaction, was found to retard the speed of the reduction.

Williams has, upon these experiments, founded a simple and expeditious process for determining the nitric and nitrous acid in water analysis, which, when used with skill, may be applied to by far the greater number of waters with which the analyst is usually called upon to deal. The requisite copper-zinc couple is prepared in the following manner:—The zinc employed should be clean, and for the sake of convenience should be in the form of foil or very thin sheet. It should be introduced into a flask or bottle, and covered with a solution of copper sulphate, containing about 3 per cent. of the crystallized salt, which should be allowed to remain upon it until a copious, firmly adherent coating of black copper has been deposited. This deposition should not be pushed too far, or the copper will be so easily detached that the couple cannot be washed without impairing its activity. When sufficient copper has been deposited the solution should be poured off, and the conjoined metals washed with distilled water. The wet couple is then ready for use.

To use this couple for the determination of nitrates it should be made in a wide-mouthed stoppered bottle. After washing, it is

* *J. C. S.* 1881, 100, and *Analyst*, 1881, 36.

soaked with distilled water ; to displace this, it is first washed with some of the water to be analyzed, and the bottle filled up with a further quantity of the water. The stopper is then inserted, and the bottle kept in a warm place for a few hours. If the bottle be well filled and stoppered, the temperature may be raised to 30° C., or even higher, without any fear of losing ammonia. The reaction will then proceed very rapidly ; but if it be desired to hasten the reaction still more, a little salt* should be added (about 0·1 gm. to every 100 c.c.), or if there be any objection to this, the water may have carbonic acid passed through it for a few minutes before it is poured upon the couple. In the case of calcareous waters, the same hastening effect may be obtained, and the lime may at the same time be removed by adding a very little pure oxalic acid to the water before digesting it upon the couple. Williams has shown that nitrous acid always remained in the solution until the reaction was finished. By testing for nitrous acid the completeness of the reaction may be ascertained with certainty, and perhaps the most delicate test that can be applied for this purpose is that of Griess, in which metaphenylene-diamine is the reagent employed. When a solution of this substance is added to a portion of the fluid, and acidified with sulphuric acid, a yellow colouration is produced in about half an hour if the least trace of a nitrate be present. The reaction easily detects one part of nitrous acid in ten millions of water. When no nitrous acid is found, the water is poured off the couple into a stoppered bottle, and, if turbid, allowed to subside. A portion of the clear fluid, more or less according to the concentration of the nitrates in the water, is put into a Nessler glass, diluted if necessary, and titrated with Nessler's re-agent in the ordinary way.

This process may be used for the majority of ordinary waters—for those that are coloured, and those that contain magnesium or other substances sufficient to interfere with the Nessler reagent, a portion of the fluid poured off the couple should be put into a small retort, and distilled with a little pure lime or sodium carbonate, and the titration of the ammonia performed upon the distillates.

About one square decimetre of zinc should be used for every 200 c.c. of a water containing five parts or less of nitric acid in 100,000. A larger proportion should be used with waters richer in nitrates. The couple, after washing, may be used for two or three waters more. When either carbonic or oxalic or any other acid has been added to the water, a larger proportion of Nessler reagent should be employed in titrating it than it is usual to add. 3 c.c. to 100 of the water are sufficient in almost all cases.

Blunt† points out that the above process may be used without distillation, and with accuracy, in the case of any water, by adding

* Dr. McGowan (Report on Analysis of Sewage and Sewage Effluents) states that "The addition of sodium chloride, to accelerate the action of the couple, is absolutely necessary ; if it be omitted, the figure obtained for nitrate in a well-nitrated effluent will almost certainly be too low."

† *Analyst*, vi. 202.

oxalic acid to a double quantity of the sample, dividing, and using one portion (clarified completely by subsidence in a closely stoppered bottle) as a comparison liquid for testing against the other, which has been treated with the copper-zinc couple, When dilution is used it must be done in both portions equally. This plan possesses the advantages that an equal turbidity is produced by Nessler in both portions, and any traces of ammonia contained in the oxalic acid will have the error due to it corrected.

A convenient method for this process is mentioned by Keating Stock as follows:—A wide-mouthed stoppered bottle holding about 200 c.c. is filled nearly to the neck with granulated zinc. Water is added, then a few drops of sulphuric acid (1 to 3) and 10 c.c. of 3 per cent. solution of copper sulphate. The stopper is inserted, and the bottle is vigorously shaken for one minute, during which time the stopper is held by a finger, and the operation is performed over the sink. The stopper is now removed, and the mouth of the bottle is covered with a piece of soft copper gauze. The couple is then thoroughly washed at the tap and drained. 100 c.c. of the water to be analyzed are placed in the bottle; the stopper is securely inserted, and the arrangement is allowed to stand at rest at a temperature of from 20 to 25° C. for 48 hours. The test is completed by thoroughly shaking the bottle, drawing off 50 c.c. of the water, adding this to 200 c.c. of ammonia-free water in a retort or flask, running in 5 c.c. saturated sodium carbonate, distilling and nesslerizing as usual. This process has been found correct between the limits of 0·086 and 4·181 grains of nitric nitrogen per gallon, when pure potassium nitrate was used in solution in ammonia-free distilled water. The couple when washed and recoppered is again ready for use. These couples will last for many months, and their convenience will be obvious to any one who has had to clean and prepare a number of zinc foils at one operation. It will be well to add that *all* new stoppered bottles intended for this purpose should have their stoppers carefully reground into the necks with a little fine emery and dilute sulphuric acid.

In calculating the amount of nitric acid contained in a water from the amount of ammonia obtained in this process, deductions must of course be made for any ammonia pre-existing in the water, as well as for that derived from any nitrous acid present.

8. Colorimetric Methods.

Phenol-Sulphonic Acid Method (**Sprengel**).—This method is applicable chiefly to waters where only small proportions of nitric acid or nitrates are to be determined, nitrites are not affected by it. The solutions required are—

Standard potassium nitrate.—0·722 gm. of KNO_3 is dissolved in a litre of water. 1 c.c. of this solution = 0·1 mgm. of N. 100 c.c. of it should be diluted to a litre for use in the actual analysis, and

10 c.c. taken ($=\frac{1}{10}$ mgm. N), to avoid the possible error resulting from measuring only 1 c.c.

Phenol-Sulphonic Acid.—Mix together two parts by measure of phenol* and five parts of pure concentrated sulphuric acid, and heat in a porcelain basin on the water-bath for about six hours. When cool, add $1\frac{1}{2}$ volumes of water and $\frac{1}{2}$ volume strong hydrochloric acid to each volume of the phenol-sulphonic acid.

Convenient quantities are 80 c.c. phenol, 200 c.c. H_2SO_4; 420 c.c. water and 140 c.c. HCl, producing 840 c.c. of a light brown solution, which is ready for immediate use.

According to Chamot and Pratt the phenol-sulphonic acid contains phenol—2 : 4—disulphonic acid, together with small quantities of p—phenol-sulphonic acid.

METHOD OF PROCEDURE: 10 c.c. of the water under examination and 10 c.c. of the standard potassium nitrate are pipetted into two small beakers and placed near the edge of a hot plate. When nearly evaporated they are removed to the top of the water-oven and left there till they are evaporated to complete dryness. As this operation usually takes about an hour and a half, it is better, when time is an object, to evaporate to dryness in a platinum dish over steam. The residue in each case is then treated with 1 c.c. of the phenol-sulphonic acid, and the beakers are placed on the top of the water-oven. If the water under examination contain a large quantity of nitrates the liquid speedily assumes a red colour, which, in a good water, will not appear for about ten minutes. After standing for fifteen minutes the beakers are removed, the contents of each washed out successively into a 100 c.c. measuring glass, a slight excess (about 20 c.c. of 0·96) of ammonia† added, the 100 c.c. made up by the addition of water, and the yellow liquid transferred to a Nessler glass. The more strongly coloured liquid is then partly transferred to the measuring glass again and the tints compared a second time. In this way the tints are adjusted, and when, as far as possible, matched, the liquid that has been partially removed is made up to the 100 c.c. mark with water, and, after well mixing, finally compared. If not exactly the same, a new liquid can at once be made up, probably of exactly the same tint, as the first experiment gives very nearly the number of c.c., of the one equivalent to the 100 c.c. of the other. A. E. Johnson in his very useful *Analyst's Laboratory Companion* (p. 82) has given a table for obtaining the nitrogen in parts per 100,000, and also in grains per gallon, by this method.

In the case of very good waters, 20, 50, or more c.c. should be evaporated to a small bulk, rinsed into a small beaker, and evaporated to dryness and treated as above—only 5 c.c. of the standard potassium nitrate ($=0{\cdot}5$ N in 100,000) being taken. In the case of very bad waters, 10 c.c. should be pipetted into a 100 c.c. measuring flask and made up to the mark with distilled water, then 10 c.c. of the well mixed liquid ($=1$ c.c. original water) withdrawn and treated as above.

It has for a long time been thought that the yellow colour produced as described above was due to the presence of trinitrophenol or picric acid, but Chamot and Pratt‡ have recently isolated the yellow compound and found it to consist of tripotassium 6—nitrophenol—2 : 4—disulphonate $NO_2\ C_6H_2\ (SO_3K)_2$. OK, $1\frac{1}{2}H_2O$ (where potash is added instead of ammonia). They found that picric acid is not formed except in minute traces.

According to A. H. Gill‖ this process does not give the nitrogen present as nitrite, since nitrosophenol C_6H_4 (NO) (OH) is formed and this is colourless in dilute solutions.

This method is not affected by the presence of chlorides.§

* Calvert's No. 2 Medical Carbolic Acid answers well.

† Caustic potash solution answers equally well.

‡ *J. Amer. Chem. Soc.* 1909, 922, & 1910, 630 ‖ *J. S. C. I.* 1895, **14**, 71.

§ *Analyst*, 1910, **35**, 81.

9. Determination of Nitrites by Griess's Method.—100 c.c. of the water are placed in a Nessler glass, and 1 c.c. each of metaphenylene-diamine $C_6H_4(NH_2)_2$, and dilute acid (p. 442) added. If colour is rapidly produced the water must be diluted with distilled water free from N_2O_3, and other trials made. The dilution is sufficient when colour is plainly seen at the end of one minute. The weak point of the process is that the colour is progressively developed; however, this is of little consequence if the comparison with standard nitrite is made under the same conditions of temperature, dilution, and duration of experiment. Twenty minutes is a sufficient time for allowing the colours to develop before final comparison.

M. W. Williams* obviates the uncertainty of the comparison tests by using colourless Nessler tubes, 30 mm. wide and 200 mm. long, graduated into millimetres. They are used as follows:—A rough comparison of the water to be examined with the standard nitrite is first made; the glasses are then filled to the same height, and the test added, and allowed to stand a few minutes. Usually one will be somewhat deeper in colour than the other. The height of the more deeply coloured liquid is read off on the scale, and a portion removed with a pipette, until the colours correspond. The amount of N_2O_3 in the shortened column is taken as equal to the other, when a simple calculation will show the amount sought. Stokes's colorimeter is useful for this purpose.

10. Determination of Nitrites by the Griess-Ilosvay Method.—This method, originally devised by Griess, has been improved by Ilosvay, who introduced the use of acetic acid instead of a mineral acid; the colour so produced is more intense and more rapidly developed. The test depends on the formation of a pink azo-dye by the action of nitrous acid on a mixture of naphthyamine and sulphanilic acid. The following solutions are required:—

(1) 1 gram of sulphanilic acid ($C_6H_4NH_2SO_3H$) is dissolved, with the aid of heat, in 14·7 gm. of glacial acetic acid mixed with an equal bulk of water. Then more water is added gradually to the warmed liquid, with constant stirring, till 285 c.c. have been used altogether.

(2) 0·2 gm. of α-naphthylamine ($C_{10}H_7NH_2$) is dissolved, with the aid of heat, in 14·7 gm. of glacial acetic acid mixed with twice its bulk of water; then more water is added until 325 c.c. have been used altogether.

These two solutions are kept separately and when mixed in equal volumes form the Griess-Ilosvay solution, which should be made only when required. The latter on keeping tends to become pink, owing to the development of nitrite in the solution from ammonia in the air; it is not affected by light.

This test is almost too delicate to be used quantitatively, but it may be done as follows:—

* *Analyst*, 1881, 38.

5 c.c. of standard nitrite solution (1 c.c. =0·01 mgm. N_2O_3) are mixed with 45 c.c. of pure distilled water in a Nessler glass, and 2 c.c. of the Griess-Ilosvay solution added.

In a similar Nessler glass 50 c.c. of the water to be examined are placed and 2 c.c. of the mixed solutions added.

Both are allowed to stand for 15 minutes before the pink colours are compared. Then the comparison is made as described in the metaphenyline-diamine method (9).

For the determination of nitrous nitrogen in sulphuric acid a standard solution is prepared as follows:—

0·0493 gm. of pure sodium nitrite, which contains 0·01 gm. of N, is dissolved in 100 c.c. water, and 10 c.c. of this solution is added drop by drop to 90 c.c. of pure sulphuric acid; the resulting mixture contains $\frac{1}{100}$ mgm. of nitrous nitrogen in a perfectly stable form. Two Nessler glasses are used, and each receives 1 c.c. of the standard solution, 40 c.c. of water, and about 5 gm. of solid sodium acetate. To one of these is added 1 c.c. of the standard solution and to the other 1 c.c. of the acid to be tested, then both are well mixed, and after 10 minutes the colours compared. If they do not correspond, the more strongly coloured liquid is diluted up to the point where the colour corresponds and the percentage of nitrous nitrogen is calculated from the amount of dilution.

11. Determination of Nitrites by Potassium Iodide and Starch.—Ekin* has pointed out that this well-known test will give the blue colour with nitrous acid in a few minutes, when the proportion is one part in ten millions; in twelve hours when one part in a hundred millions; and in forty-eight hours when one in a thousand millions. Experience has proved that waters charged with much organic matter must be clarified by the addition of a little pure alum, then well agitated and filtered before testing.

Ekin used acetic acid for acidifying the water to be tested, and blank experiments with pure water were simultaneously carried on. Sulphuric or hydrochloric acid will, no doubt, give a sharper reaction, but both these acids are more liable to contain impurities affecting the reaction than is the case with pure acetic acid. Owing to the instability of alkali iodides, zinc iodide, which is not open to this objection, is now generally used.

12. Determination of Suspended Matter.—Filters of Swedish paper, about 110 mm. in diameter, are packed one inside another, about 15 or 20 together, so that water will pass through the whole group, moistened with dilute hydrochloric acid, washed with hot distilled water until the washings cease to contain chlorine, and dried. The ash of the paper is thus reduced by about 60 per cent., and must be determined for each parcel of filter-paper by inc nerating 10 filters, and weighing the ash. For use in determining suspended matter, these washed filters must be dried for several hours at 120-130° C., and each one then weighed at intervals of an hour until the weight ceases to diminish, or at least until the loss of weight between two consecutive weighings does not exceed 0·0003 gm. It is most convenient to enclose the filter during weighing in two short tubes, fitting closely one into the other. The closed ends of test tubes, 50 mm. long, cut off by leading a crack

* Pharm. Trans. 1881, 286.

round with the aid of a pastille or very small gas jet, the sharp edges being afterwards fused at the blow-pipe, answer perfectly. Each pair of tubes should have a distinctive number, which is marked with a diamond on both tubes. In the air bath they should rest in grooves formed by a folded sheet of paper, the tubes being drawn apart, and the filter almost, but not quite, out of the smaller tube. They can then be shut up whilst hot by gently pushing the tubes together, being guided by the grooved paper. They require to remain about twenty minutes in a desiccator to cool before weighing. Filtration will be much accelerated if the filters be ribbed before drying. As a general rule, it will be sufficient to filter a quarter of a litre of a sewage, half a litre of a highly polluted river, and a litre of a less polluted water ; but this must be frequently varied to suit individual cases. Filtration is hastened, and trouble diminished, by putting the liquid to be filtered into a narrow-necked flask, which is inverted into the filter, being supported by a funnel-stand, the ring of which has a slot cut through it to allow the neck of the flask to pass. With practice the inversion may be accomplished without loss, and without previously closing the mouth of the flask. When all has passed through, the flask should be rinsed out with distilled water, and the rinsings added to the filter. Thus any particles of solid matter left in the flask are secured, and the liquid adhering to the suspended matter and filter is displaced. The filtrate from the washings should not be added to the previous filtrate, which may be employed for determination of total solid matter, chlorine, hardness, etc.

Thus washed, the filter with the matter upon it is dried at 100° C., then transferred from the funnel to the same pair of tubes in which it was previously weighed, dried at 120°-130° C. and weighed repeatedly until constant. The weight thus obtained, minus the weight of the filter and tubes, gives the weight of the total suspended matter dried at 120°-130° C.

To ascertain the quantity of mineral matter in this, the filter with its contents is incinerated in a platinum crucible, and the total ash thus determined, minus the ash of the filter alone, gives the weight of the mineral suspended matter.

13. Determination of combined Chlorine.—To 50 c.c. of the water in a porcelain dish or glass flask add two or three drops of solution of potassium chromate (**D.** ii), so as to give it a faint tinge of yellow, and add gradually from a burette standard solution of silver nitrate (**D.** i), until the red silver chromate which forms after each addition of the nitrate ceases to disappear on stirring or shaking. The number of c.c. of silver solution employed will express the chlorine present as chloride in parts in 100,000. If this amount be much more than 10, it is advisable to take a smaller quantity of water.

If extreme accuracy be necessary, after completing a determination, destroy the slight red tint by an excess of a soluble chloride, and repeat the determination on a fresh quantity of the water in

a similar flask placed by the side of the former. By comparing the contents of the flasks, the first tinge of red in the second flask may be detected with great accuracy. It is absolutely necessary that the liquid examined should not be acid, unless with carbonic acid, nor more than very slightly alkaline. It must also be colourless, or nearly so. These conditions are generally found in waters, but, if not, they may be brought about in most cases by rendering the liquid just alkaline with lime water (free from chlorine), passing carbonic anhydride to saturation, boiling, and filtering. The calcium carbonate has a powerful clarifying action, and the excess of alkali is exactly neutralized by the carbonic anhydride. If this is not successful, the water must be rendered alkaline, evaporated to dryness, and the residue gently heated to destroy organic matter. The chlorides may then be extracted with water, and determined in the ordinary way either gravimetrically or volumetrically.

14. Determination of Hardness.*—The following method, devised by the late Dr. Thomas Clark, of Aberdeen, is in general use. It serves to measure more particularly the soap-destroying power of waters and its indications are most useful. The test requires to be carefully performed and should never be done in a hurry, especially in the case of magnesian waters. Both the standardization of the soap solution and the determination of the hardness of a water should be carried out strictly according to the following directions. Before commencing the determination, however, the total solid matter present in a water should be weighed as it gives a useful *approximate* idea of how much to use for the soap test. Although no rule can be given, the total hardness in many waters is about half the total solids, and the sample may be so diluted, if necessary, as to bring it within the limit mentioned below. Thus, if a water contains 50 grains of solids per gallon take 25 c.c. for hardness.

Measure 50 c.c. of the water, or, if necessary, a less quantity (usually 25 or 10 c.c., together with 25 or 40 c.c. of recently boiled and cooled distilled water) into a well-stoppered bottle of about 250 c.c. capacity, shake briskly for a few seconds, and suck the air from the bottle by means of a glass tube, in order to remove any carbon dioxide which may have been liberated from the water. Then run in from a burette standard soap solution (**E** ii), one c.c. at a time at first and about 0·5 c.c. towards the end of the operation, shaking vigorously after each addition, until a lather is obtained, which, when the bottle is laid at rest on its side, remains persistent for 5 minutes. Waters containing much magnesium salts give a false lather after the addition of only a few c.c. of soap solution; this, however, disappears entirely on allowing the bottle to remain for several minutes on its side after an extra vigorous shaking. Such waters must always be so diluted that not more than 7 c.c. of the soap solution are required to

* For the determination of hardness of waters by titration, see p. 74.

Results of Analysis expressed

Number of Sample.	DESCRIPTION.	REMARKS.
	Upland Surface Waters.	
I.	The Dee above Balmoral, March 9th, 1872	Clear .. .. .
II.	Glasgow Water supply from Loch Katrine—average of monthly analyses during five years, 1876—81	Clear ; very pale brow
III.	LiverpoolWatersupply fromRivingtonPike,June4th,1869	Clear .. .. .
IV.	Manchester Water supply, May 9th, 1874	Turbid .. .
V.	Cardiff Water supply, Oct. 18th, 1872	Clear .. .. .
	Surface Water from Cultivated Land.	
VI.	Dundee Water supply, March 12th, 1872	Turbid; brownish yell
VII.	Norwich Water supply, June 18th, 1872	Slightly turbid .
	Shallow Wells.	
VIII.	Cirencester, Market Place, Nov. 4th, 1870	Slightly turbid .
IX.	Marlborough, College Yard, Aug. 22nd, 1873	Clear .. .. .
X.	Birmingham, Hurst Street, Sept. 18th, 1873	Clear; strong saline tast
XI.	Sheffield, Well near, Sept. 27th, 1870	Very turbid & offen sive. Swarmin with bacteria, &
XII.	London, Aldgate Pump, June 5th, 1872	Clear .. .. .
XIII.	London, Wellclose Square, June 5th, 1872	Slightlyturbid;salineta
XIV.	Leigh, Essex, Churchyard Well, Nov. 28th, 1871 ..	Slightly turbid .
	Deep Wells.	
XV.	Birmingham, Short Heath Well, May 16th, 1873 ..	Clear .. .. .
XVI.	Caterham, Water Works Well, Feb. 14th, 1873 ..	Clear .. .. .
	Ditto, Softened (Water supply)	.. ..
XVII.	London, Albert Hall, May, 1872	Slightly turbid .
XVIII.	Gravesend, Railway Station, Jan. 17th, 1873	Clear .. .. .
	Springs.	
XIX.	Dartmouth Water supply, Jan. 8th, 1873	Turbid.. .. .
XX.	Grantham Water supply, July 11th, 1873	Clear .. .. .
	London Water supply—average monthly analyses during 21	**years, 1869—89.**
XXI.	From the Thames	.. ..
XXII.	From the Lea	.. ..
XXIII.	From Deep Chalk Wells (Kent Company)	.. ..
XXIV.	Ditto(ColneValleyCo.)softened—thirteen years,1877—89	.. ..
XXV.	Ditto (Tottenham)—thirteen years, 1877—89	.. ..
XXVI.	***Birmingham Water supply—average monthly analyses, 18**	**75—1880.**
	Average Composition of Unpolluted Water.	
XXVII.	Rain Water .. .. 39 samples	.. ..
XXVIII.	Upland Surface Water .. .. .. 195 ,,	.. ..
XXIX.	Deep Well Water .. .. 157 ,,	.. ..
XXX.	Spring Water .. .. 198 ,,	.. ..
XXXI.	Sea Water .. .. 23 ,,	.. ..
	Sewage.	
XXXII.	Average from 15 "Midden" Towns, 37 analyses ..	.. ..
XXXIII.	Average from 16 "Water Closet" Towns, 50 analyses	.. ..
XXXIV.	Salford, Wooden Street Sewer, March 15th, 1869 ..	.. ..
XXXV.	Merthyr Tydfil, average 10 a.m. to 5 p.m., Oct. 20th, 1871 (after treatment with lime)	.. ..
XXXVI.	Ditto, Effluent Water	.. ..

* This is the old supply, not the Welsh water with which Birmingham is now supplied.

in parts per 100,000.

tal lid ter.	Organic Carbon.	Organic Nitrogen.	Organic $\frac{C}{N}$	Nitrogen as Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Inorganic Nitrogen.	Total Combined Nitrogen.	Chlorine.	Hardness. Temporary.	Hardness. Permanent.	Hardness. Total.
1·52	·132	·014	9·4	0	0	0	·014	·50	0	1·5	1·5
2·94	·148	·016	9·2	0	·005	·005	·022	·64	—	—	·9
·66	·210	·029	7·2	·002	0	·002	·031	1·53	·3	3·7	4·0
·00	·132	·031	4·1	·002	0	·002	·033	·90	0	2·7	2·7
·50	·212	·031	6·8	0	·034	·034	·065	1·40	7·1	12·9	20·0
1·16	·418	·059	7·1	·001	·081	·082	·141	1·75	0	6·0	6·0
0·92	·432	·080	5·4	·012	·048	·036	·128	3·10	21·3	5·3	26·6
1·00	·041	·008	5·1	0	·362	·362	·370	1·60	18·4	4·6	23·0
2·48	·049	·015	3·3	0	·613	·613	·628	1·90	15·6	10·1	25·7
0·20	·340	·105	3·2	·511	14·717	15·228	15·333	36·50	27·5	99·6	127·1
8·50	1·200	·126	9·5	·091	0	·091	·217	2·20	2·0	1·4	3·4
3·10	·144	·141	1·0	·181	6·851	7·032	7·173	12·85	37·1	40·0	77·1
6·50	·278	·087	3·2	0	25·840	25·840	25·927	34·60	26·7	164·3	191·0
2·12	·210	·065	3·2	0	5·047	5·047	5·112	13·75	14·3	45·7	60·0
5·08	·009	·004	2·2	0	·447	·447	·451	1·30	4·6	5·1	9·7
7·68	·028	·009	3·1	0	·021	·021	·030	1·55	15·2	6·0	21·2
8·80	·015	·003	5·0	—	—	—	—	—	—	—	4·4
1·68	·168	·042	4·0	·007	·066	·073	·115	15·10	3·4	2·2	5·6
8·00	·127	·029	4·4	·063	2·937	3·000	3·029	5·40	27·9	14·5	42·4
7·36	·060	·016	3·7	0	·330	·330	·346	2·45	1·6	10·0	11·6
0·20	·048	·018	2·7	0	·833	·833	·851	2·05	17·1	6·5	23·6
8·02	·191	·033	5·8	0	·210	·210	·243	1·68	—	—	20·1
8·99	·134	·025	5·4	0	·226	·226	·251	1·76	—	—	20·9
1·50	·049	·011	4·5	0	·446	·446	·458	2·47	—	—	28·5
4·40	·059	·014	4·2	·003	·367	·370	·384	1·70	—	—	6·0
1·39	·068	·016	4·2	·054	·143	·196	·196	2·85	—	—	23·3
6·01	·245	·054	4·6	·002	·231	·233	·287	1·73	7·7	8·8	16·5
2·95	·070	·015	4·7	·024	·003	·027	·042	·22	—	—	·3
9·67	·322	·032	10·1	·002	·009	·011	·043	1·13	1·5	4·3	5·4
3·78	·061	·018	3·4	·010	·495	·505	·523	5·11	15·8	9·2	25·0
8·20	·056	·013	4·3	·001	·383	·384	·397	2·49	11·0	7·5	18·5
98·7	·278	·165	1·7	·005	·033	·038	·203	1975·6	48·9	748·0	796·9
									Suspended Matter. Mineral.	Suspended Matter. Organic.	Suspended Matter. Total.
82·4	4·181	1·975	2·1	4·476	0	4·476	6·451	11·54	17·81	21·30	39·11
72·2	4·696	2·205	2·1	5·520	·003	5·523	7·728	10·66	24·18	20·51	24·69
19·6	11·012	7·634	1·4	5·468	0	5·468	13·102	20·50	18·88	26·44	45·32
9·20	1·282	·952	1·3	1·054	·052	1·106	2·058	5·25	7·88	6·56	14·44
3·48	·123	·031	4·0	·048	·300	·348	·379	2·60		Trace.	

produce a permanent lather. In other cases the addition of soap solution may be continued until not more than 16 c.c. are required to produce a permanent lather, which in all cases is attained when, on rolling the bottle half-way round after 5 minutes standing, the lather still covers the whole surface without breaking. The burette is then read and the hardness ascertained from Table 7, the results being multiplied by 2 or 5 when 25 or 10 c.c. of the water, diluted to 50 c.c., have been used.

It is very important to note that even when the hardness of a water is approximately known, or when making a duplicate determination, the soap solution must always be added in c.c.'s (or less) at a time, with shaking after each addition, and never in large quantities.

When water containing calcium and magnesium carbonates, held in solution by carbonic acid, is boiled, carbonic anhydride is expelled, and the carbonates precipitated. The hardness due to these is said to be *temporary*, whilst that due to calcium and magnesium sulphates, chlorides, etc., and to the amount of their carbonates soluble in pure water (the last-named being about three parts per 100,000) is called *permanent*.

To determine *permanent hardness*, a known volume of the water (say 100 c.c.) is boiled gently for half an hour in a flask, the mouth of which is freely open. The level of the water should be marked by an ink or blue pencil mark on the flask, and hot water added from time to time to make up the loss by evaporation. At the end of half an hour, close the flask with a glass marble and cool to ordinary temperature, then make up to the original volume by addition of recently boiled and cooled distilled water, filter through a dry filter, and determine the hardness in the filtrate. The hardness thus found, deducted from that of the unboiled water, will give the *temporary* hardness.

According to Prof. H. Jackson*: "Every gallon of pure water requires about 10 grains of ordinary soap before a lather can be produced, and each degree of hardness will necessitate the addition of another quantity of 10 grains of soap."

15. Mineral Constituents and Metals.—The quantities of the following substances which may be present in a sample of water are subject to such great variations that no definite directions can be given as to the volume of water to be used. The analyst must judge in each case from a preliminary experiment what will be a convenient quantity to take.

Sulphuric Acid.—Acidify a litre or less of the water with hydrochloric acid, concentrated on the water-bath to about 100 c.c. and while still hot add a slight excess of barium chloride. Filter, wash, ignite, and weigh as barium sulphate, or determine volumetrically, as on p. 349.

* Cantor Lectures on Detergents and Bleaching Agents used in Laundry Work, 1907.

Sulphuretted Hydrogen.—Titrate with a standard solution of iodine, as on p. 348.

Phosphoric Acid.—This substance may be determined in the solid residue obtained by evaporation, by moistening it with nitric acid, and again drying to render silica insoluble ; the residue is again treated with dilute nitric acid, filtered, molybdic solution added, and set aside for twelve hours in a warm place ; filter, dissolve the precipitate in $2\frac{1}{2}$ % ammonia, precipitate with magnesia mixture, and weigh as magnesium pyrophosphate, or determine volumetrically as on p. 307 et seq.

Another method is to add to 500 c.c. of the sample about 10 c.c. of solution of alum, then a few drops of ammonia, lastly acidify slightly with acetic acid, and set aside to allow the precipitated $AlPO_4$ to settle. The clear liquid may then be poured off, the precipitate dissolved in nitric acid and determined with molybdic solution.

These determinations are only possible in cases where the P_2O_5 is very large. In most waters it is simply necessary to record whether the molybdic precipitate is in heavy or minute traces.

Silicic Acid.—Acidify a litre or more of the water with hydrochloric acid, evaporate, and dry the residue thoroughly. Then moisten with hydrochloric acid, dilute with hot water, and filter off, wash, ignite, and weigh the separated silica.

Iron. To the filtrate from the determination of silicic acid add a few drops of nitric acid, dilute to about 100 c.c., and determine by colour titration, as on p. 238 ; or where the amount is large, add a slight excess of ammonia, and heat gently for a short time. Filter off the precipitate and determine the iron in the washed precipitate colorimetrically.

Calcium.—To the filtrate from the iron determination add excess of ammonium oxalate, filter off the calcium oxalate, ignite and weigh as calcium carbonate or as lime, or determine volumetrically with permanganate as on p. 172.

Magnesium.—To the concentrated filtrate from the calcium determination add sodium phosphate (or, if alkalies are to be determined in the filtrate, ammonium phosphate), and allow to stand for twelve hours in a warm place. Filter, ignite the precipitate, and weigh as magnesium pyrophosphate, or, without ignition, titrate with uranium.

Barium. Is best detected in a water by acidifying with hydrochloric acid, filtering perfectly clear if necessary, then add a clear solution of calcium sulphate, and set aside in a warm place. Any white precipitate which forms is due to barium.

Potassium and Sodium.—These are generally determined jointly, and for this purpose the filtrate from the magnesium determination may be used. Evaporate to dryness, and heat gently to expel ammonium salts, remove phosphoric acid with lead acetate, and

the excess of lead in the hot solution by ammonia and ammonium carbonate. Filter, evaporate to dryness, heat to expel ammonium salts, and weigh the alkalies as chlorides.

It is, however, generally less trouble to employ a separate portion of water. Add to a litre or less of the water enough pure barium chloride to precipitate the sulphuric acid, boil with pure milk of lime, filter, concentrate, and remove the excess of lime with ammonium carbonate and a little oxalate. Filter, evaporate, and weigh the alkali chlorides in the filtrate. If the water contains but little sulphate, the barium chloride may be omitted, and a little ammonium chloride added to the solution of alkali chlorides.

If potassium and sodium must each be determined, separate the potassium by means of platinic chloride; or, after weighing the mixed chlorides, determine the *chlorine* present in them, and calculate the amounts of potassium and sodium by the following formula :—Calculate all the chlorine present as potassium chloride; deduct this from the weight of the mixed chlorides, and call the difference d. Then as 16·1 : 58·46 : : d : NaCl present. (See also p. 144.) Or the sodium chloride may be determined by Fenton's method, p. 65.

Lead.—May be determined by the method proposed by Miller. Acidulate the water with two or three drops of acetic acid, and add $\frac{1}{20}$ of its bulk of saturated aqueous solution of sulphuretted hydrogen. Compare the colour thus produced in the colorimeter, or a convenient cylinder, with that obtained with a known quantity of a standard solution of a lead salt, in a manner similar to that described for the determination of iron (p. 238). The lead solution should contain 0·1831 gm. of normal crystallized lead acetate in a litre of distilled water, and therefore each c.c. contains 0·0001 gm. of metallic lead.

It is obvious that in the presence of copper or other heavy metals the colour produced by the above method will all be ascribed to lead; it is preferable, therefore, to adopt the method of Harvey,* in which the lead is precipitated as chromate. The results, however, are not absolute as to quantity, except so far as the eye may be able to measure the amount of precipitate.

The standard lead solution is the same as in the previous method. The precipitating agent is pure potassium dichromate, in fine crystals or powder.

250 c.c. or so of the water are placed in a Phillips's jar with a drop or two of acetic acid, and a few grains of the reagent added, and agitated by shaking. One part of lead in a million parts of water will show a distinct turbidity in five minutes or less. In six or eight hours the precipitate will have completely settled, and the yellow clear liquid may be poured off without disturbing the sediment, which may then be shaken up with a little distilled water, and its quantity judged by comparison with a similar experiment made with the standard lead solution.

* *Analyst*, **6**, 146.

Copper.—Determine by colour titration, as on p. 204.

Arsenic.—Add to half a litre or more of the water enough sodium hydrate, free from arsenic, to render it slightly alkaline, evaporate to dryness, and extract with a little concentrated hydrochloric acid. Introduce this solution into the generating flask of a small Marsh's apparatus, and pass the evolved hydrogen, first through a U-tube filled with pumice, moistened with lead acetate, and then through a piece of hard glass tube about 150 mm. in length, and 3 mm. in diameter (made by drawing out combustion tube). At about its middle, this tube is heated to redness for a length of about 20 mm. by the flame of a small Bunsen burner, and here the arseniuretted hydrogen is decomposed, arsenic being deposited as a mirror on the cold part of the tube. The mirror obtained after the gas has passed slowly for an hour is compared with a series of standard mirrors obtained in a similar way from known quantities of arsenic. Care must be taken to ascertain in each experiment that the hydrochloric acid, zinc, and whole apparatus are free from arsenic, by passing the hydrogen slowly through the heated tube before introducing the solution to be tested. The best form of apparatus (Marsh-Berzelius) is that which is now used for detecting and determining small quantities of arsenic in beer, malt, etc. An electrolytic form of apparatus is also largely used.

Zinc.—This metal usually exists in waters as bicarbonate, and on exposure of such waters in open vessels a film of zinc carbonate forms on the surface; this is collected on a platinum knife or foil and ignited. The residue is of a yellow colour when hot, and turns white on cooling. The reaction is exceedingly delicate. Potassium ferrocyanide produces a turbidity in such waters owing to the insolubility of zinc ferrocyanide. The reagent will detect 1 part of zinc in 2,000,000 of water.

DETERMINING THE HARDNESS OF WATERS.

The method as arranged by Hehner is described on p. 74, but a paper read before the Yorkshire section of the Society of Chemical Industry, by H. R. Procter, proposes a somewhat modified method leading in many cases to greater accuracy. The following is a part of that paper as written by him.* The greater part has relation to the technical plans of water softening for steam boilers and other purposes.

Hehner titrates the temporary or bicarbonate hardness with $^{N}/_{10}$ HCl, using methyl orange as an indicator, which is practically insensitive to carbonic acid, The method gives very exact results if certain precautions are taken. Methyl orange is the sodium salt of a colour acid of moderate strength, and the change from the yellow salt condition to the red colour of the free acid marks the end point, which is sharp and exact when working with strong mineral acids, and with normal solutions. Even in this case it is desirable to use the smallest

* *J. S. C. I.* **23**, 1904, 8.

possible amount of the indicator, but, in working with $^N/_{10}$ solutions, the amount of acid required to completely decompose the colour salt becomes very perceptible, and the change from yellow to red is not instantaneous, but passes through orange to pink with the consumption of an appreciable amount of acid. Thus it was found that, using a 10 gm. per litre solution of the indicator in 25 c.c. of water freed from carbonic acid by previous boiling, the following quantities of $^N/_{10}$ HCl were required to produce a clear pink:—8 drops of methyl orange solution = 1·5 c.c., 4 drops = 0·5 c.c., 2 drops = 0·5 c.c. As even 0·5 c.c. in titrating 100 c.c. of water would correspond to 2·5 parts of hardness per 100,000, and there is always a question as to what particular colour corresponds to the neutral point, the following procedure may be recommended. To 100 c.c. of distilled water, one drop, or some other definite quantity of the indicator is added, and titrated to orange, or to the tint to the change of which the eye of the individual operator is most sensitive. The water of which the hardness is to be determined is similarly titrated with the same quantity of indicator, and in a similar beaker, until it exactly matches the distilled water. and from the amount of acid so used the quantity is deducted as a correction which was required to produce the same colour change with distilled water only. The results so obtained accurately correspond with those got by using alizarin as an indicator in boiling solution, though in the latter method the end reaction is sharper. It may be noted that methyl orange is not absolutely unaffected by carbonic acid, a somewhat crocus-yellow being attained instead of the lemon yellow reached with pure boiled water, but the difference is insufficient to interfere with its satisfactory use as an indicator.

Hehner's method for the determination of permanent hardness is less satisfactory than the foregoing. It consists in evaporating 100 c.c. of the water to dryness with a known excess, say 20 c.c., of $^N/_{10}$ sodium carbonate solution, taking up the soluble matter with cold distilled water, filtering off the precipitated calcium carbonate and magnesia on a small filter, washing the precipitate with cold water and titrating back the excess of sodium carbonate in the filtrate with methyl orange or rosolic acid as indicator. With lime-hardness only, and with the precautions above described, the method may be pronounced fairly satisfactory; with magnesia, it is well not merely to evaporate to dryness but to slightly heat the residue to thoroughly decompose any magnesium carbonate present, and even then the washing should not be excessive, as calcium carbonate is soluble to the extent of 3 parts per 100,000, and magnesia to about 2·5 parts. A more accurate, as well as a more rapid, method is to employ a fair excess of sodium carbonate, and to make up the solution to a known volume, say 100 c.c., and pipette off an aliquot part for titration, as the presence of excess of sodium carbonate materially reduces the solubility both of calcium and magnesium carbonates. Both these methods, however, should be superseded, where really accurate work is required, by those introduced by Pfeifer and Wartha.* That for the determination of temporary hardness is identical with that of Hehner, except that, in place of methyl orange, a drop of a mixture of about 1 gm. of the purest alizarin paste in 200 c.c. of distilled water is employed. This indicator is surprisingly sensitive; even more so I think than phenolphthalein, but as it is unfortunately affected by carbon dioxide, it is necessary to complete the titration at a boiling temperature. The change is from violet in alkaline solution (perhaps slightly varying in shade with the nature of the particular base present) to a perfectly clear pale lemon-yellow when neutral or acid. The titration of the water should be done with $^N/_{10}$ HCl or H_2SO_4 in a silver, platinum, or hard porcelain basin. The acid should be added in the cold till the violet shade gives place to a clean yellow, and the liquid then brought to a boil, when, with the escape of carbonic acid, the violet colour will return, and should at once be destroyed by the addition of another drop of the acid, and so on, until no further change of colour takes place. It is undesirable to boil the indicator long, especially in an alkaline condition, as a violet deposit is formed on the sides of the basin, presumably of calcium and magnesium alizarates, which can only be dissolved by excess of acid, and is thus apt to cause perceptible errors. In place of titrating to exact neutrality, the acid may be added in very small excess, and the whole of the liberated carbon dioxide

* *Z. a. C.*, 1902, 198.

boiled off at once, and the solution then brought back to neutrality by $^N/_{10}$ NaOH, the solution boiled for a moment, and the titration completed. The results in either case are exact, a fraction of a drop of alkali changing the clear lemon colour to a dirty yellow. If 100 c.c. of water are used, multiplication of the c.c. of acid by 5 gives the temporary hardness in parts of $CaCO_3$ per 100,000. The boiling must in no case take place in an ordinary glass beaker or flask, as an amount ol alkali is dissolved which may lead to serious inaccuracy. Even hard Jena glass is not free from this effect, though the amount dissolved is so small that for most practical purposes it may be neglected. The following experiment will illustrate the point. 100 c.c. of distilled water boiled for an hour (with additions to maintain the volume) in a Berlin porcelain basin showed an alkalinity or colour-change with alizarin ; in a Jena flask a perceptible change of colour was visible, but pure yellow was restored with one drop of $^N/_{10}$ acid, while when boiled in an ordinary Bohemian flask, 0·4 c.c. of acid was consumed, and if the neutralized liquid were boiled further it again became alkaline, and further additions of acid were required, so that no coincident results could be obtained. With the precautions named, the results with a known solution of hydric calcic carbonate containing only 5·5 parts of temporary hardness, and whether titrated alone or with additions of magnesium sulphate, were accurate within one part in 100,000, and experiments with other quantities were equally satisfactory.

In the determination of permanent hardness, Pfeifer and Wartha, in addition to the use of alizarin as indicator, have introduced the important improvement of replacing the sodium carbonate of Hehner's method by a mixture of equal parts of $^N/_{10}$ sodium carbonate and hydroxide solutions. While, as has been already explained, sodium carbonate perfectly precipitates calcium salts as carbonates on merely boiling, it becomes necessary to evaporate to dryness and to heat whenever any magnesium salt is present, in order to convert magnesium carbonate into oxide, since magnesium carbonate is not sufficiently insoluble. In presence of sodium hydroxide, however, the magnesium carbonate is at once converted into magnesium hydroxide, and perfectly efficient precipitation is obtained by merely boiling for some time with sufficient excess of the reagent. A good excess, say 50 per cent. or more, is essential, not only because it is impossible to say before analysis what proportion of sodium carbonate and what of caustic will be required, but because the presence of the CO_3 ions of the sodium carbonate in the solution greatly lessens the solubility of the calcium carbonate, and similarly the OH ions of the sodium hydroxide lessen that of the magnesium hydroxide. Unless the water is extremely hard, 50 c.c. of the $^N/_{10}$ mixed solution to 200 c.c. of water is a convenient and sufficient quantity. The mixture may be boiled until reduced within 200 c.c. in a platinum or porcelain basin, or, more conveniently, and with no material loss of accuracy, in a 300 c.c. Jena flask, but on no account in ordinary Bohemian glass. Even the Jena flask will become perceptibly etched at the water line if used repeatedly. The solution, after cooling, is made up to 200 c.c. with distilled water in a gauged flask, and allowed to stand till the precipitated bases have settled, and 100 c.c. is pipetted or siphoned off and titrated. As the quantity named corresponds to 100 c.c. of the original water, and 25 c.c. of $^N/_{10}$ alkali, the difference between the acid actually used and 25 c.c. will correspond to the amount of alkali neutralized by the acids of the permanent hardness, and multiplied by 5 will give the latter in terms of mgms. per 100,000 calculated as calcium carbonate. The temporary hardness will also be precipitated, but, containing no fixed acids, will not interfere. Pfeifer employs the water which has been neutralized in the titration of temporary hardness, in place of the original water. In this case the result obtained will represent total hardness, from which the permanent hardness is obtained by deducting the temporary. In place of allowing the precipitate to settle, the solution may be filtered through a small filter, which is carefully washed with the solution, of which the first 50 c.c. or so is rejected, as filters are rarely absolutely free from acidity or alkalinity, and, even if at first perfectly neutral, easily absorb acids or ammonia from the laboratory air, unless very carefully protected. Many irregularities occurred in the determinations until this source of error was detected. 15 cm. filters of three different makes were macerated with hot distilled water, and proved in all

cases alkaline to methyl orange and acid to phenolphthalein, the difference between the two indicators, + or −, amounting in each case to about 0·75 c.c. of $^N/_{10}$ solution.* A case must now be considered which is not very infrequent in waters of this district. It occasionally happens that in the determination of permanent hardness, a larger quantity of acid is required to neutralize the mixture than corresponds to the volume of $^N/_{10}$ alkali which has been added, and that therefore the permanent hardness would appear as a minus quantity. This somewhat puzzling result is due to the presence of sodium carbonate in the original water, which in this case can have no permanent hardness other than that due to the solubility of calcium carbonate, which cannot be removed by softening, but which is not reckoned in the above methods of analysis, though it is counted in the soap test. Where sodium carbonate is thus found, a proportionate amount must be deducted from the temporary hardness. If the total hardness after neutralization is determined by Pfeifer's method, the presence of sodium carbonate will be indicated by the total hardness coming out as less than the temporary, the difference being obviously the alkalinity due to the soda; each part of hardness corresponding to 1·06 part of sodium carbonate. Since in the ordinary methods of water softening lime is precipitated as carbonate, but magnesia as oxide, with the consumption of a double quantity of caustic lime or caustic alkali, it is impossible from hardness-determinations alone to calculate the materials required for softening, or the actual weights of the bases titrated, so long as it is uncertain whether or in what proportion magnesia is present. Pfeifer determines this in the following manner:—100 c.c. of the water is neutralized with $^N/_{10}$ acid in presence of alizarin, in boiling solution, exactly as in the determination of temporary hardness, which may be combined with that of magnesia. A known quantity of clear limewater (25 or 50 c.c.), which should be at least 50 per cent. in excess of that required for precipitating the magnesia present, is measured into a 200 c.c. flask, the hot neutralized solution is rinsed in with boiling distilled water free from carbonic acid, and made up with the latter to 5 c.c. above the mark to allow of contraction in cooling; the flask is tightly corked or stoppered, and well shaken to mix, for which purpose the neck above the mark must be a long one, and set aside to cool and settle. Though not essential, it probably increases the completeness of the precipitation if the corked flask is heated for half an hour or so on the water-bath. I prefer to allow sufficient time for the liquid to completely clear, and to pipette off 100 c.c. to titrate back with $^N/_{10}$ acid, which may be done, cold with phenolphthalein, or hot with alizarin with equal accuracy. Pfeifer filters, but in this case the strength of the limewater must be determined by a blank experiment conducted in exactly the same way with distilled water; and it is better to reject the first 50 c.c. in each case to avoid error from want of neutrality of the filter-paper, and great care must be taken to filter rapidly, to avoid possibilities of carbonation by the atmosphere, for which purpose a suction filter with a perforated porcelain disc covered with a neatly-fitted disc of filter-paper answers well. If, on the other hand, the liquid is settled and pipetted, the risk of carbonation is so small that an equal quantity of the same limewater may be measured direct, and titrated, using the same indicator as has been employed for the water, phenolphthalein in the cold being on the whole preferable. Deducting the $^N/_{10}$ acid required for the mixture of limewater and water from that employed for the limewater alone, and multiplying the difference by five, gives the hardness due to magnesia in terms of mgms. of calcium carbonate per 100,000, from which actual Mg may be reckoned by multiplying by 0·24; or MgO multiplying by 0·4. Carefully conducted, the method is extremely exact, its accuracy being quite equal to that of the determination of hardness, and probably superior to that of any gravimetric method for such minute quantities. The theory of the process is that, while calcium hydrate will precipitate magnesia, it has no action on lime salts; and a good excess of lime serves not only to quicken the reaction but to diminish the solubility of the magnesia. If iron is present it will of

* In confirmation of this defect in filter papers Lenormand has given the history of some experiments with various papers (*C. N.* lxxxix. 229), and comes to the conclusion that in the analysis of either fresh or salt waters they should never be filtered but allowed time to settle clear, and in that state used in the analysis of waters for dissolved organic matters.

course be reckoned with the magnesia, and should be determined colorimetrically with thiocyanate (also a process of great accuracy for small quantities), and deducted. It may be assumed that it is present in the ferric state, and that therefore 0·24 of Mg. corresponds to 0·3733 of Fe. Aluminium, if present, would behave like iron, any traces of alumina dissolved by lime having no effect (on phenolphthalein at least), but it is rare that more than traces of alumina exist in natural waters, though it would have to be reckoned with in river-waters receiving manufacturing effluents, and its determination would not be particularly easy. Possibly a colorimetric method with alcoholic extract of logwood or some other mordant dyestuff might be devised where the water was required for dyeing, but it is not likely that it would introduce any material error into water-softening calculations, and it would be removed with the other impurities. Having determined the magnesia, or, more strictly, the acid with which it and any other bases are combined which are precipitated by lime, it becomes possible to calculate the calcium present in the water, by deducting the magnesia-hardness from the total hardness, and calculating the remainder into Ca by multiplication by 0·4. The carbon dioxide present as hydric carbonate is given in parts per 100,000 by multiplication of the temporary hardness by 0·88 for CO_2 or 1·2 for CO_3. When the proportion of hardness due to magnesia is known, it is possible to calculate the quantities of lime and sodium carbonate required for softening, since magnesium salts, as has been stated, cannot be satisfactorily removed as carbonates, but must be converted into hydroxides by lime or some other caustic alkali; and this applies to the permanent hardness which is converted into carbonate by sodium carbonate, as well as to the bicarbonate reduced to carbonate by lime. Thus each equivalent of magnesia present requires an additional equivalent of lime beyond that required by the corresponding calcium salt. Pfeifer gives a formula for this purpose, calculated for German degrees of hardness, which are reckoned in parts per 100,000 of CaO instead of parts of $CaCO_3$ as is customary in France and England. I have, therefore, taken the liberty of transposing it into terms of parts of $CaCO_3$ per 100,000. Ht in the formula signifies temporary, and Hp permanent hardness, and Hm hardness due to magnesia, whether temporary or permanent. The quantities given are in mgms. per litre, gms. per cubic metre, or lb. per 100,000 gallons of the water to be treated. $5{\cdot}6\ (Ht + Hm)$ = lime (CaO) required; $10{\cdot}6\ Hp$ = dry sodium carbonate; or $28{\cdot}6\ Hp$ = soda crystals ($Na_2CO_3 . 10H_2O$). If only temporary hardness is to be softened by liming only, the quantity required is $5{\cdot}6\ (Ht + Hm - Hp)$ if Hm is larger than Hp, but if not, only the temporary hardness need be taken into account. Finally, for softening with sodium hydroxide and sodium carbonate only, which is sometimes convenient for small boiler installations, we have $8\ (Ht + Hm)$ = NaOH required; $10{\cdot}6\ Hp - (Ht + Hm)$ = Na_2CO_3 required. Consequently, if the water has less permanent hardness than the sum of the temporary and magnesia hardness, it cannot be softened completely in this way without leaving excess of sodium carbonate in the water.

Some waters contain large quantities of dissolved free carbon dioxide in addition to the "half-combined" present as temporary hardness, and though this is not included in any hardness determination, it, of course, combines with and renders useless an equivalent quantity of the lime added for softening, and must, therefore, be taken into account in reckoning the lime required. The free CO_2 is easily determined by a method described on p. 100. 100 c.c. of the water is titrated slowly with N/10 solution of Na_2CO_3 and phenolphthalein, till a tinge of permanent pink is produced, when the number of c.c. used, multiplied by 2·2, will give the parts of CO_2 per 100,000, or with multiplication by 2·8 will give the weight of lime required to remove it. Of course, such a determination is of no use unless there is some security that the sample of water really represents the average, and has not lost carbonic acid by exposure. The reaction depends on the fact that sodium bicarbonate is neutral to phenolphthalein, while the normal carbonate is alkaline. It must be remembered that the theoretical quantity of precipitants does not always give the best practical results, owing to difficulties of settling and filtration, and in some cases it is necessary to be content with less than the theoretical softening (see Archbutt and Deeley, *J.S.C.I.*, 1891, 511).

METHODS OF DETERMINING THE ORGANIC IMPURITIES IN WATER WITHOUT GAS APPARATUS.

THE foregoing methods of estimating the organic impurities in potable waters, though very comprehensive and trustworthy, yet possess the disadvantage of occupying a good deal of time, and necessitate the use of a complicated and expensive set of apparatus, which may not always be within the reach of the operator.

No information of a strictly reliable character as to the nature of the organic matter or its quantity can be gained from the use of standard permanganate solution as originally devised by Forchammer, and the same remark applies to the loss on ignition of the residue, both of which have been in past time largely used.

The Forchammer or oxygen process, however, as improved by Letheby, and further elaborated by Tidy, may be considered as worthy of considerable confidence in determining the amount of organic substances contained in a water.

The Oxygen Absorption Process.

For the Preparation of the Reagents required *see p.* 444.

This process depends upon the determination of the amount of oxygen required to oxidize the organic and other oxidizable matters in a known volume of water, slightly acidified with pure sulphuric acid. For this purpose, a standard solution of potassium permanganate is employed in excess. The amount of unchanged permanganate, after a given time, is ascertained by means of a solution of sodium thiosulphate, by the help of the iodine and starch reaction.

Tidy and Frankland in all cases made a blank experiment with pure distilled water side by side with the sample, and this procedure has been adopted generally.

Two tests are usually made, viz., the amount of oxygen absorbed in three minutes and in four hours respectively. The former, which practically gives the amount absorbed instantaneously, affords a means of differentiating between one class of oxidizable substance and another, and, in the case of sewages and effluents, affords an excellent method, in conjunction with the incubator, of determining the amount of putrefaction which is taking place. In the case of waters, an immediate reduction of permanganate may be caused by such reducing agents as nitrites, ferrous salts, or sulphuretted hydrogen, and Tidy was disposed to attribute this reduction, in the known absence of iron and sulphuretted hydrogen, to nitrites.

The process is carried out as follows :—

The vessels used for this determination should be rinsed with sulphuric acid and then with water. 12-oz. stoppered flasks or

500 c.c. W.M. bottles answer well. First measure out into each flask 10 c.c. of the dilute sulphuric acid, then 10 c.c. of the permanganate, and finally 250 c.c. of distilled water for the blank and the same quantity of each of the samples to be tested. The whole of the vessels are then placed in water at 80° F., or in an incubator, and maintained at that temperature for four hours. The flasks should be examined at intervals, and if the pink colour becomes much diminished a further 10 c.c. of permanganate should be added. In all cases a good excess of permanganate should be maintained during the whole of the four hours ; the flasks should also be shaken occasionally. At the end of four hours add to each a few drops of the potassium iodide solution till the clear yellowish-brown colour of iodine replaces the pink of the permanganate. Now run in from a burette the standard solution of thiosulphate with occasional shaking till the colour of the solution is reduced to a pale yellow, then add a few drops of starch solution and more thiosulphate till the blue colour disappears.

Ex. 1. 250 c.c. of water treated as above required 22·4 c.c. thiosulphate ; the blank took 32·5 c.c.

$$\cdot 4\left(\frac{32\cdot5-22\cdot4}{32\cdot5}\right)=0\cdot124 \text{ parts of oxygen absorbed per 100,000 of water.}$$

Ex. 2. Suppose that a sewage effluent required the addition of 30 c.c. of permanganate to maintain a good pink colour, and that 28·1 c.c. of thiosulphate were needed (blank as before), then

$$\cdot 4\left(\frac{32\cdot5\times3-28\cdot1}{32\cdot5}\right)=0\cdot854 \text{ parts of oxygen absorbed per 100,000 of effluent.}$$

To calculate "grains per gallon" instead of "parts per 100,000," use the factor 0·28 instead of 0·4 in the above formulae.

The three minutes' test is carried out as follows :—

Ten c.c. of the permanganate solution and the same volume of the dilute sulphuric acid are measured into a small stoppered bottle of about 100 c.c. capacity, and the latter is carefully warmed in a water-bath to the temperature of 80° F. A portion of the sample (sewage, effluent, etc.) is warmed separately to the same temperature, and 25 c.c. of it (or 10 c.c., diluted to 25 c.c. with distilled water, in the case of a very strong sewage) are added to the acid permanganate. The contents of the bottle are mixed by gentle rotation, and after three minutes' standing potassium iodide is added and the titration finished as described above. In the case of waters, 250 c.c. are measured into a flask or bottle, such as is used for the four hours' test, warmed in a water-bath to 80° F., the acid and permanganate added, etc., as above.

Dupré* carried out a number of experiments with this process and arrived at the following conclusions :—

(1) That, practically no decomposition of permanganate takes place during four hours when digested in a closed vessel at 80° with perfectly pure water and the usual proportion of pure sulphuric

* *Analyst*, 1882, 7, 1.

acid. By adopting the closed vessel, all dust or reducing atmospheric influence is avoided.

(2) The standardizing of the thiosulphate and permanganate, originally and from time to time, must be made in a closed vessel in the same manner as the analysis of a water, since it has been found that when the titration is made slowly in an open beaker less thiosulphate is required than in a stoppered bottle. This is probably due to a trifling loss of iodine by evaporation.

(3) That with very pure waters no practical difference is produced by a rise or fall of temperature, the same results being obtained at 32° F. as at 80° F. On the other hand, with polluted waters, the greater the organic pollution, the greater the difference in the amount of oxygen absorbed according to temperature.

(4) As to time, it appears that very little difference occurs in good waters between three and four hours' digestion; but with bad waters there is often a very considerable increase in the extra hour; and thus Dupré doubts whether even four hours' digestion suffices for very impure waters.

Dupré in further comment on the temperature at which it is advisable to carry out this method (*Analyst* x. 118), and also as to the reactions involved, points out one feature which has in all probability impressed itself upon other operators, that is to say, the effect of chlorides when present in any quantity. It is evident that if in this case the permanganate is used at a high temperature and in open vessels, chlorine will be liberated; part escaping into the air, and the rest nullifying the reducing effect of any organic matter present on the permanganate. If, however, the experiment be conducted at high temperature in a closed vessel, the probable error is eliminated, because the chlorine is retained, and subsequently, when cool and the potassium iodide added, the free Cl liberates exactly the same amount of iodine as would have been set free by the permanganate from which it was produced. It thus becomes possible to determine the amount of oxidizable organic matter, even in sea water. In order, however, to reduce the probable error from the presence of chlorides, Dupré prefers to carry on the experiment at a very low temperature, in fact, as near 0° C. or 32° F. as possible, and uses phosphoric acid in place of sulphuric (250 gm. glacial acid to the litre; 10 c.c. of which is used for each quarter or half litre of water). The sample is cooled, the reagent added in a stoppered bottle, and kept in an ordinary refrigerator for twenty-four hours. The same operator very rightly condemns the practice adopted by some chemists, especially those of Germany, of boiling a water with permanganate and sulphuric acid. The presence of chlorides in varying proportions must in such case totally vitiate the results.

Comparison of the Results of this Process with the Combustion Method.—I cannot do better than quote Frankland's remarks on this subject, as contained in his treatise on *Water Analysis*.

"The objections to the oxygen process are first, that its indications are only comparative, and not absolute; and, second, that its comparisons are only true when the organic matter compared is substantially identical in composition.

"For many years, indeed, after this process was first introduced, the action of the permanganate was tacitly assumed to extend to the complete oxidation of the organic matter in the water, and, therefore, the result of the experiment was generally stated as 'the amount of oxygen required to oxidize the organic matter;' whilst some chemists even employed the number so obtained to calculate the actual weight of organic matter in the water on the assumption that equal weights of all kinds of organic matter required the same weight of oxygen for their complete oxidation.

"Both these assumptions have been conclusively proved to be entirely fallacious, for it has been experimentally demonstrated, by operating upon known quantities of organic substances dissolved in water, that there is no relation either between the absolute or relative weight of different organic matters and the oxygen which such matters abstract from permanganate.

"Nevertheless, in the periodical examination of waters from the same source, I have noticed a remarkable parallelism between the proportions of organic carbon and of oxygen abstracted from permanganate. Thus, for many years past, I have seen in the monthly examination of the waters of the Thames and Lea supplied to London such a parallelism between the numbers given by Tidy expressing 'oxygen consumed,' and those obtained by myself in the determination of 'organic carbon.'

"This remarkable agreement of the two processes, extending as it did to 1,418 out of 1,686 samples, encouraged me to hope that a constant multiplier might be found, by which the 'oxygen consumed' of the Forchammer process could be translated into the 'organic carbon' of the combustion method of analysis. To test the possibility of such a conversion, my pupil, Woodland Toms, made, at my suggestion, the comparative experiments recorded in the following tables:

I.—River Water.

Source of Sample.	Oxygen consumed $\times \frac{C}{O} =$	Organic carbon by combustion.
Chelsea Company's Supply	0·098 × 2·6 =	0·256
West Middlesex Co's ,, ...	0·116 × 2·5 =	0·291
Lambeth Co.'s ,, ...	0·119 × 2·43 =	0·282
Southwark Co.'s ,, ...	0·121 × 2·22 =	0·269
New River Co.'s ,, ...	0·076 × 2·4 =	0·183
Chelsea Co.'s second sample	0·070 × 2·69 =	0·188
Lambeth Co.'s ,, ...	0·119 × 1·99 =	0·234
New River Co.'s ,, ...	0·107 × 2·25 =	0·221

"As the result of these experiments the average multiplier is 2·38, and the maximum errors incurred by its use would be—0·021 part of organic carbon in the case of the second example of the Chelsea Company's water, and +0·049 part in that of the second sample of the Lambeth Company's water. These errors would have practically little or no influence upon the analyst's opinion of the quality of the water. It is desirable that this comparison should be extended to the water of other moderately polluted rivers.

II.—Deep Well Water.

Source of Sample.	Oxygen consumed, $\times \frac{C}{O} =$	Organic carbon by combustion.
Kent Company's Supply	0·015 × 5·1 =	0·077
Colne Valley Co.'s ,, ...	0·0133 × 6·9 =	0·094
Hodgson's Brewery well	0·03 × 5·3 =	0·158

"The relation between 'oxygen consumed' and 'organic carbon' in the case of deep well waters is thus very different from that which obtains in the case of river waters, and the average multiplier deduced from the foregoing examples is 5·8, with maximum errors of +0·01 of organic carbon in the case of the Kent Company's water, and—0·015 in that of the Colne Valley water. Such slight errors are quite unimportant.

"Similar comparative experiments made with shallow well and upland surface waters showed amongst themselves a wider divergence, but pointed to an average multiplier of 2·28 for shallow well water, approximately the same as that found for moderately polluted river water, and 1·8 for upland surface water.

"In the interpretation of the results obtained, either by the Forchammer or combustion process, the adoption of a scale of organic purity is often useful to the analyst, although a classification according to such a scale may require to be modified by considerations derived from the other analytical data. It is indeed necessary to have a separate and more liberal scale for upland surface water, the organic matter of which is usually of a very innocent nature, and derived from sources precluding its infection by zymotic poisons.

"Subject to modification by the other analytical data, the following scale of classification has been suggested by Tidy and myself:—

Section I.—Upland Surface Water.

"**Class I.** *Water of great organic purity,* absorbing from permanganate not more than 0·1 part of oxygen per 100,000 parts of water, or 0·07 grain per gallon.

"**Class II.** *Water of medium purity,* absorbing from 0·1 to 0·3 part of oxygen per 100,000 parts of water, or 0·07 to 0·21 grain per gallon.

"**Class III.** *Water of doubtful purity,* absorbing from 0·3 to 0·4 part per 100,000, or 0·21 to 0·28 grain per gallon.

"**Class IV.** *Impure water,* absorbing more than 0·4 part per 100,000 or 0·28 grain per gallon.

Section II.—Water other than Upland Surface.

"**Class I.** *Water of great organic purity,* absorbing from permanganate not more than 0·05 part of oxygen per 100,000 parts of water, or 0·035 grain per gallon.

"**Class II.** *Water of medium purity,* absorbing from 0·05 to 0·15 part of oxygen per 100,000, or 0·035 to 0·1 grain per gallon.

"**Class III.** *Water of doubtful purity,* absorbing from 0·15 to 0·2 part of oxygen per 100,000, or 0·1 to 0·15 grain per gallon.

"**Class IV.** *Impure water,* absorbing more than 0·2 part of oxygen per 100,000, of 0·15 grain per gallon.

Determination of Free and Saline Ammonia and of Albuminoid Ammonia (Wanklyn).

(For the preparation of Reagents required, see p. 437).

Measure 500 c.c. of the water to be examined into a stoppered retort or a 32 oz. round-bottomed Bohemian flask with a rubber stopper, the vessel used being sufficiently large to prevent any of the sample being spirted over into the condenser.* Add a small quantity of recently-ignited sodium carbonate and connect by an india-rubber joint with a Liebig's or other condenser, which should be thoroughly rinsed out with good tap-water immediately before use. The distillation should be conducted as rapidly as is compatible with a certainty that no spirting takes place, and a stream of water should be passed through the condenser during the whole of the distillation. When 100 c.c. have distilled over, the receiver (a stoppered 100 c.c. flask) is changed and the distillation continued till another 50 c.c. have been collected in a Nessler glass.

* Thorpe's well-known "Revenue Still" is very compact and answers well for water and sewage distillation.

The latter is then tested at once with 2 c.c. of Nessler's solution, and if no colour is produced, which is most usually the case, the distillation is stopped. If a colour is produced, further portions are collected and tested till ammonia ceases to come over. In this way the **free and saline ammonia** are obtained.

Whilst the distillation has been going on, 50 c.c. of alkaline permanganate and about 25 c.c. of distilled water are together boiled in a nickel dish or a flask for a few minutes to expel any ammonia. This is then poured into the flask and the distillation continued, the distillate being collected in a 100 c.c. flask followed by successive portions in Nessler glasses till the evolution of ammonia has ceased. The ammonia thus collected forms the **albuminoid ammonia.**

The respective distillates are now "Nesslerized" as follows:—Transfer each 100 c.c. distillate to a Nessler glass, add 4 c.c. of Nessler's solution, and mix well with a long glass tube having a bulbed end. The colour that develops enables an approximate estimate to be made of the amount of ammonia present, and one or more standards are made up with ammonium chloride and ammonia-free water as quickly as possible, 4 c.c. of Nessler's solution added to each, and after mixing all are allowed to stand at least ten minutes, so that the colour may fully develop and all may acquire the room temperature, this latter being a matter of importance. The final adjustment is made by pouring some of the more strongly-coloured liquid into a 100 c.c. measuring cylinder until a perfect match of tints is obtained, or a Stokes's Colorimeter may be used. The mode of calculation is best shown by an example.

Ex. 500 c.c. of water distilled.

Free and saline ammonia. 1st 100 c.c. 85 c.c. gave the same colour as a standard made up of 0·5 c.c. standard NH_4Cl solution (1 c.c. $=0{\cdot}00005$ gm. NH_3). 2nd 50 c.c. None.

Result, $\frac{100}{85} \times 0{\cdot}005 = 1{\cdot}18 \times {\cdot}005$

$= 0{\cdot}0059$ parts free and saline ammonia per 100,000.

Albuminoid ammonia. 1st 100 c.c. was such that 90 c.c. of a standard containing 0·8 c.c. NH_4Cl solution in the 100 c.c. was equal to it in colour. 2nd 50 c.c. none.

Result, $\frac{90}{100} \times {\cdot}008 = 0{\cdot}0072$ parts of albuminoid ammonia per 100,000.

(With 500 c.c. water distilled, 1 c.c. of the standard NH_4Cl solution $=0{\cdot}01$ parts NH_3 per 100,000 of water.)

In the case of **sewages** and **tank effluents** take 50 or 100 c.c. according to strength, add 500 c.c. of pure water, or of good tap-water of which the free and albuminoid ammonia are known, then a little Na_2CO_3 and distil till 200 c.c. have been collected in

a stoppered flask. Then add 50 c.c. of alkaline permanganate and 100 c.c. of tap-water, also 3 pieces of ignited pumice to prevent bumping and continue the distillation until another 200 c.c. have been collected. Dr. Mc Gowan* states that: "In actual practice this distillation is never carried further than the 200 c.c., no matter at what rate the albuminoid ammonia may be coming off when this limit is reached. The estimation is thus only approximate, at least in the case of a sewage or an ordinary effluent. If the distillation of this was carried further (with the addition of successive quantities of ammonia-free water to the retort), albuminoid ammonia would be obtained for an indefinite period in gradually decreasing amounts in the successive fractions of the distillate." Suitable fractions of the distillates are then diluted with ammonia-free water to 100 c.c. and Nesslerized. For good filter and land effluents take 250 c.c. and 250 c.c. of tap-water, but if bad 100 c.c. or less and 500 c.c. of tap-water should be used.

Determination of Organic Nitrogen in Sewages or Effluents by the Kjeldahl Process.

Dr. Mc Gowan† proceeds as follows :—

From 10 c.c. to 100 c.c. of the sample (according to its strength, are boiled down with 4 c.c. of sulphuric acid (free from nitrogen) in a round-bottomed Jena flask, the heating being continued) after all the water has been evaporated off, until the acid becomes colourless—the mouth of the flask being closed by a balloon stopper as soon as the acid begins to fume. When cold, the flask is rinsed out with distilled water into a stoppered measuring flask, a few c.c. of a solution of oxalate of potash (ammonia-free) being sometimes added to throw down the lime present. The solution is then rendered *just* alkaline with purified potash, and filled up to the mark with water. The flocculent precipitate which invariably forms upon the addition of the potash, both in the presence and absence of oxalate, is allowed to subside for at least twenty-four hours, and a suitable fraction of the clear liquid is then Nesslerized.

A " blank " is made in exactly the same way, substituting distilled water for sewage or effluent. The nitrogen found in the " blank " is then corrected for the minute quantity of nitrogen in the distilled water added before boiling down. The corrected "blank" thus obtained, representing the unoxidized nitrogen in the 4 c.c. of sulphuric acid used, is then subtracted from the corresponding one in the actual determination, the difference giving the organic nitrogen *plus* the nitrogen from the free and saline ammonia present. Finally, by deducting the

* Royal Commission on Sewage Disposal. Vol. IV. Part V. Dr. Mc. Gowan's Report on methods of chemical analysis as applied to Sewage and Sewage Effluents, 1904 (p. 14).

† Report on Methods of Chemical Analysis of Sewage and Effluents. Vol. IV., Part V. of the Fourth Report of the Royal Commission on Sewage Disposal, 1904.

latter—determined, if possible, by direct Nesslerization of the sample—the organic nitrogen present is obtained. As a rule direct Nesslerization for free and saline ammonia is impracticable, owing to the turbidity produced on adding Nessler's solution. (Dr. Mc Gowan also describes a more elaborate process "with reduction," for details of which the reader is referred to the blue-book already mentioned.)

Dr. G. J. Fowler* gives the following process :—

30 c.c. of the sample are placed in an 8 oz. flask, a little sodium carbonate added, and it is then distilled with steam till the distillate shows no indication of free ammonia. The steam is generated in a 32-oz. flask and passed into the flask containing the sample. This flask should be heated by a Bunsen burner to prevent the steam condensing in it. In this way the sample is concentrated to about 5 c.c. and is then transferred to an 8-oz. Jena flask with a long neck and 20 c.c. of pure H_2SO_4 (free from Nitrogen) added. The mixture is carefully heated over a naked Bunsen flame in the draught chamber for about half an hour, a little phosphoric anhydride (P_2O_5) is then added, and the heating continued till the mixture is quite clear. After allowing to cool somewhat the mixture is poured into about 200 c.c. of water, and after complete cooling made up exactly to 250 c.c. ; 50 c.c. of this solution are then taken, made alkaline with a saturated solution of caustic soda, 500 c.c. of tap-water added, and the ammonia distilled off and Nesslerized in lots of 100 c.c. A "blank" should be made with 35 c.c. of distilled water and all reagents as above, and allowed for. The organic ammonia thus found is always higher than the albuminoid ammonia, and the relation between the two has been found to vary within fairly wide limits with different samples. In the Fifth Report of the Royal Commission on Sewage Disposal† it is stated that "The ratio of albuminoid to total nitrogen in an effluent is usually from 1 : 2 to 1 : 3, though it may in certain cases be either below or above those figures. When an effluent contains a large quantity of suspended solids, the ratio tends to be high."

Method of Procedure for Mossy or Peaty Waters.

R. R. Tatlock and R. T. Thomson‡ have contributed a paper on this subject and the following is a portion of it :—

CHLORIDES.—The determination of these seldom presents any difficulties, the titration with standard silver nitrate, and the employment of potassium chromate as indicator, being usually sufficient. Difficulties arise, however, when we have to deal with mossy or peaty waters and with waters containing acids or iron salts. With mossy waters, which are also sometimes acid, we have found the best mode of dealing to consist in adding some calcined magnesia (magnesium oxide) to a portion (not necessarily measured) of the water, and

* *Sewage Works Analyses*, p. 58. † Cd. 4278. 1908, p. 223.

‡ *J. S. C. I.* **23**, 428.

agitating thoroughly for a few minutes. In this way acid, if present, is neutralized, and the mossy or peaty matter is precipitated and removed from solution, while the magnesia remains practically insoluble. All that is then necessary is to filter through a dry filter, and titrate a portion of the decolorized water with standard silver nitrate.

Acid waters are treated with magnesia as just described, and so are waters containing iron, but in the latter case a few drops of hydrogen peroxide should be added in order to convert any ferrous compounds into the ferric condition. The magnesia then removes the iron wholly, and it only remains to filter the mixture and determine the chlorides in the solution as before.

Nitrates and Nitrites.—The determination of nitrates in a water is in our opinion one of the greatest importance, at least in the case of water intended for dietetic purposes, and therefore an accurate and speedy method is of great value. We have come to the conclusion that, when properly adapted, the phenol-sulphonic acid method (p. 468) is decidedly the most handy and reliable. In natural waters, however, there are two ingredients which are fatal to a correct determination of nitrates, namely, organic matters, especially the brown mossy or peaty organic matter, which is so often present in the waters we are familiar with in Scotland, and the chlorides of magnesium and sodium. For the removal of organic colouring matters, such as is found in mossy waters, there is nothing superior to agitation with calcined magnesia as already described under the determination of chlorine. We have found that when chlorine is present to the extent of 3·5 grs. per gallon (5 parts per 100,000) of chloride of sodium, only about 60 per cent. of the whole is obtained, and when 21 grs. per gallon (30 parts per 100,000) are present, only about 34 per cent. is obtained. These proportions are, however, only roughly approximate, as we have found that the results in presence of the same proportion of chlorides are somewhat erratic. In order to obviate this adverse influence of the chlorides, Mason recommends the use in the standard of the same proportion of chlorides as is present in the water being tested, so as to counterbalance their influence; but owing to the somewhat erratic effect of the chlorides we came to the conclusion that it would be more satisfactory to remove them entirely. For this purpose we have applied and adapted the method which is employed for the removal of chlorides from crude glycerine in testing the strength of that article by the dichromate method. This consists in agitating the sample with excess of silver oxide, which removes the chlorine in the form of silver chloride. When treated in this way, however, a considerable proportion of silver remained in solution, apparently as oxide, and this was deposited on evaporation of the filtrate to dryness for treatment with phenol-sulphonic acid, which soon converted the brown silver oxide into sulphate. The silver compound seemed to have the rather unexpected effect of lowering the result for nitrates, although not nearly to the same extent as, say, 3 grs. of sodium chloride per gallon. We were thus compelled to work with a limited supply of silver oxide, adding just enough to convert all the chlorides into silver chloride, this being determined by the usual volumetric method. When this was carried out the exact proportion of nitrates present was obtained, but considerable difficulty was experienced in obtaining a clear filtrate, as traces of silver chloride passed through the filter. This difficulty was also overcome by the use of a little aluminium sulphate followed by calcined magnesia. The final method adopted was therefore as follows:—100 to 200 c.c. of the water are treated with enough silver oxide, in a fine state of division, to decompose the chlorides, the proportion of which had been previously ascertained. After agitating thoroughly, a little aluminium sulphate (say about 0·1 gr.) is dissolved in the mixture, then excess of calcined magnesia is added, and the agitation continued for a minute or two. In this way the chlorides and organic matter are entirely precipitated, and are then filtered off through a dry filter, when the filtered solution will be found as free from colour as distilled water. A portion of the filtrate (50 to 100 c.c.) is now evaporated to dryness over an open water-bath, and the residue tested for nitrates by the well-known phenol-sulphonic acid method. A number of test experiments showed that in every case the whole of the nitrates, added to a water containing com-

paratively large proportions of chlorides and organic matter, was obtained by this method of determination.

The next point which arose for consideration was the effect of nitrites on this determination, but it was clearly shown that this was almost *nil*, or that their presence only slightly raised the proportion of nitrates. This fact suggested to us the idea of applying the phenol-sulphonic acid method to the determination of nitrites also, provided these could be readily converted into nitrates. The ideal reagent was soon found in hydrogen peroxide, which suits admirably for the purpose in view. To determine the nitrites, therefore, it is only necessary to remove the chlorine from, and render colourless, a quantity of the water to be tested, exactly in the manner just described. In such dilute solutions as generally occur in waters there is no danger of any nitrite being precipitated by the silver compound. A portion of the treated water is tested for nitrates, and to an equal portion there is added a little hydrogen peroxide, and the mixture evaporated to dryness. The nitrites which existed in the water are now present in the residue in the form of nitrate, and it only remains to apply the phenol-sulphonic test, then subtract the nitrates actually present in the water as such from the total nitrates now obtained, and calculate the remainder to nitrites, or to bring these compounds to nitric and nitrous nitrogen respectively. Of course it would be advisable to make certain of the presence of nitrites by one of the well-known colour tests for these compounds.

Microscopical Examination of Deposit.—The most convenient plan of collecting the deposit is to place a circular microscopical covering glass at the bottom of a large conical glass holding about 20 oz. The glass should have no spout, and should be ground smooth on the top. After shaking up the sample, this vessel is filled with the water, covered with a plate of ground glass, and set aside to settle. After settling, the supernatant water is drawn off by a fine siphon, and the glass bearing the deposit lifted out, either by means of a platinum wire (which should have been previously passed under it), or in some other convenient way, and inverted on to an ordinary microscopical slide for examination. It is desirable to examine the deposit first by a $\frac{1}{4}$th and then by a $\frac{1}{8}$th objective. The examination should be made as soon as the water has stood overnight. If the water be allowed to stand longer, organisms peculiar to stagnant water may be developed and mislead the observer. Particular notice should be taken of bacteria, infusoria, ciliata or flagellata, disintegrated fibres of cotton, or linen, or epithelial *débris.*

It is particularly desirable to report clearly on this microscopical examination; not merely giving the general fact that organisms were present, but stating as specifically as possible the names or classes of the organisms, so that more data may be obtained for the application of the examination of this deposit to the characters of potable waters.

It is also desirable to examine the residue left on a glass slide by the evaporation of a single drop of the water. This residue is generally most conveniently examined without a covering glass. The special appearances to be noticed are the presence or absence of particles of organic matter, or organized structure, contained in the crystallized forms which may be seen; and also whether any part of the residue left, especially at the edges, is tinted more or less with green, brown, or yellow.

Method of Recording Water and Sewage Examination Results.

The report* of the committee appointed to establish a Uniform System of recording the Results of the Chemical and Bacterial Examination of Water and Sewage is as follows:—That it is desirable that results of analysis should be expressed in parts per 100,000 except in the case of dissolved gases, when these should be

* British Association Report, 1899.

stated as cubic centimetres of gas at 0° C., and 760 millimetres in 1 litre of water. This method of recording results is in accordance with that suggested by the committee appointed in 1887 to confer with the committee of the American Association for the Advancement of Science, with a view to forming a uniform system of recording the results of water analysis.

The committee suggest that in the case of all nitrogen compounds the results be expressed as parts of nitrogen over 100,000, including the ammonia expelled on boiling with alkaline permanganate, which should be termed albuminoid nitrogen. The nitrogen will therefore be returned as:

(1) Ammoniacal nitrogen from free and saline ammonia.

(2) Nitrous nitrogen from nitrites.

(3) Nitric nitrogen from nitrates.

(4) Organic nitrogen (either by Kjeldahl or by combustion, but the process used should be stated).

(5) Albuminoid nitrogen.

The total nitrogen of all kinds will be the sum of the first four determinations.

The committee are of opinion that the percentage of nitrogen oxidized—that is, the ratio of (2) and (3) to (1) and (4)—gives sometimes a useful measure of the stage of purification of a particular sample. The purification effected by a process will be measured by the amount of oxidized nitrogen as compared with the total amount of nitrogen existing in the crude sewage.

In raw sewage and in effluents containing suspended matter, it is also desirable to determine how much of the organic nitrogen is present in the suspended matter.

In sampling, the committee suggest that the bottles should be filled nearly completely with the liquid, only a small air-bubble being allowed to remain in the neck of the bottle. The time at which a sample is drawn, as well as the time at which its analysis is begun, should be noted. An effluent should be drawn to correspond as nearly as possible with the original sewage, and both it and the sewage should be taken in quantities proportional to the rate of flow when that varies (*e.g.*, in the emptying of a filter-bed).

In order to avoid the multiplication of analyses, the attendant at a sewage works (or any other person who draws the samples) might be provided with sets of twelve or twenty-four stoppered quarter-Winchester bottles, one of which should be filled every hour or every two hours, and on the label of each bottle the rate of flow at the time should be written. When the bottles reach the laboratory, quantities would be taken from each proportional to these rates of flow and mixed together, by which means a fair average sample for the twenty-four hours would be obtained.

The committee at present are unable to suggest a method of reporting bacterial results, including incubator tests, which is likely to be acceptable to all workers.

Standards for Sewage Effluents.

The following standards of purity or limits of impurity, all of which are of a somewhat arbitrary character, have from time to time been put forward as applying to effluents that it was desired to pass into streams.

Effluents are classed as good when they show no more than :—

(Mersey and Irwell Joint Committee)

1 grain per gallon of oxygen absorbed in 4 hours.
0·1 grain per gallon of albuminoid ammonia.

(Ribble Joint Committee's Inspector)

0·1 part of albuminoid ammonia per 100,000.
No suspended matter
Nitrates present.

(Derbyshire County Council)

0·1 part of albuminoid ammonia per 100,000, more than 0·5 part of nitric nitrogen per 100,000, and an effluent should be so thoroughly oxidized that it does not absorb more oxygen after incubation for one week than it does at the time of collection.

All the above, however, have now been superseded by the recommendations given in the Fifth Report of the Royal Commission on Sewage Disposal.* In this the Commissioners report that :— "The experiments which we have already made show that the mere estimation of the amount of organic matter in an effluent does not, by itself, afford a sufficiently reliable index as to the effect which that effluent will have on any stream into which it may be discharged" (par. 320). Further on we read : "According to our present knowledge, an effluent can best be judged by ascertaining, first, the amount of suspended matter which it contains, and second, the rate at which the effluent, after the removal of the suspended solids, takes up oxygen from water.

In applying this test it is important that the suspended solids should be removed, and estimated separately.

Small variations in the amount of suspended solids in effluents may seriously affect the rate at which the effluents take up oxygen, and unless these solids are first removed, the dissolved oxygen absorption test might give a misleading figure as to the character of the effluent" (par. 321).

Consequently, no arbitrary standards based on the amounts of oxygen absorbed or albuminoid ammonia are suggested by the Commissioners, and instead the Report (par. 322) proceeds :—

"For the guidance of local authorities, we may provisionally state that an effluent would generally be satisfactory if it complied with the following conditions :—

(1) That it should not contain more than three parts per 100,000 of suspended matter ; and

* Cd. 4278. Issued in 1908.

(2) That, after being filtered through paper, it should not absorb more than

(a) 0·5 part by weight per 100,000 of dissolved or atmospheric oxygen in twenty-four hours.

(b) 1·0 part by weight per 100,000 of dissolved or atmospheric oxygen in forty-eight hours; or

(c) 1·5 part by weight per 100,000 of dissolved or atmospheric oxygen in five days."

The following recent analyses* of effluents may be found useful:—

(Parts per 100,000).	Effluent from Land.	Effluent from Land.	Effluent from Bacterial Treatment.	Effluent from Bacterial Treatment.
Total solids	64·1	86·4	70·3	59·4
Suspended matter, total ..	Less than 3	Less than 3	Less than 3	4·40
,, ,, volatile ..	..	..	..	2·98
,, ,, non-volatile	..	..	..	1·42
Ammonia, free	0·58	0·53	0·95	0·22
,, albuminoid ..	0·26	0·075	0·13	0·17
Oxygen absorbed from permanganate:				
In 3 minutes at 80° F. ..	..	..	..	0·89
In 4 hours at 80° F.	0·65	0·65	1·38	2·23
Nitrogen as nitrates	1·09	1·61	2·73	1·95
,, ,, nitrites	0·015	0·04	0·02	0·03
Chlorine	6·1	7·1	6·7	5·5
Dissolved oxygen absorbed:				
(a) in 24 hours	0·3	0·0	0·0	0·02
(b) in 48 hours	0·8	0·04	0·30	0·06
(c) in 5 days	1·4	0·28	0·72	0·22

Characteristics of Waters derived from various Geological Formations.

Dr. Rideal† gives the following useful summary of the above:—

Hard Waters, as a rule, are furnished by the following formations: Calcareous strata of Silurian, Devonian or Old Red Sandstone, and Coal Measures, Mountain Limestone, Lias, Oolite, Upper Greensand, Chalk. **Soft Waters,** by Igneous, Metamorphic, non-calcareous Cambrian, Silurian, Devonian, and Coal Measures, Lower Greensand, London and Oxford Clay, Bagshot Beds (hardness 1-9, average 4), and non-calcareous gravel. Water from Gault Clay varies very much: some of it is soft and pure, some of "fair quality," hardness 9-11 degrees; in Bedfordshire it often contains much lime and iron, derived from pyrites and coprolites. Lower Greensand and shale waters are frequently very ochreous. Water from Oxford and Kimmeridge Clays contains much vegetable matter, and is sometimes bituminous; other clays often include

* From Rideal & Burgess's paper on "The New Standards for Sewage Effluents," *Analyst*, **34**, 1909, 201.

† "Water and its Purification," pp. 259-260. Detailed information on this topic is given in an appendix to the book.

much sulphate of lime and give waters of high permanent hardness. The new Red Sandstone waters are generally briny and quite unfit for drinking, besides containing much sulphate of lime and magnesium salts. Magnesian limestone (Dolomite) also yields usually a bad supply. The water in porous strata below the central portions of clay basins is usually bad, containing much alkali chloride and sulphate, and also sodium carbonate, due to the rain having percolated laterally through a large body of soil before reaching the spot, and having dissolved and accumulated the soluble constituents: from the presence of alkali carbonate the lime is generally low, and there is often little organic matter.

Rules for Converting Parts per 100,000 into Grains per Gallon, and Vice Versa.

To convert—

Parts per 100,000 into grains per gallon, multiply by 0·7.
Grains per gallon into parts per 100,000, divide by 0·7.
Grams per litre into grains per gallon, multiply by 70.

THE INTERPRETATION OF THE RESULTS OF ANALYSIS.

All figures refer to parts per 100,000.

The primary form of natural water is rain, the chief impurities in which are traces of organic matter, ammonia, and ammonium nitrate derived from the atmosphere. On reaching the ground it becomes more or less charged with the soluble constituents of the soil, such as calcium and magnesium carbonates, potassium and sodium chlorides, and other salts, which are dissolved, some by a simple solvent action, others by the agency of carbonic acid in solution. Draining off from the land, it will speedily find its way to a stream which, in the earlier part of its course, will probably be free from pollution by animal matter, except that derived from any manure which may have been applied to the land on which the rain fell. Thus comparatively pure, it will furnish to the inhabitants on its banks a supply of water which, after use, will be returned to the stream in the form of sewage charged with impurity derived from animal excreta, soap, household refuse, etc., the pollution being perhaps lessened by submitting the sewage to some purifying process, such as irrigation of land, filtration, or clarification. The stream in its subsequent course to the sea will be in some measure purified by slow oxidation of the organic matter, and by the absorbent action of vegetation. Some of the rain will not, however, go directly to a stream, but sink through the soil to a well. If this be shallow it may be considered as merely a pit for the accumulation of drainage from the immediately surrounding soil, which, as the well is in most cases close to a dwelling, will be almost inevitably charged with excretal and other refuse; so that the water when it reaches the well will be contaminated with soluble impurities thence derived, and with nitrites and nitrates resulting from their oxidation. After use the water from the well will, like the river water, form sewage, and find its way to a river, or again to the soil, according to circumstances.

In the case of a deep well, from which the surface water is excluded, the conditions are different. The shaft will usually pass through an impervious stratum, so that the water entering it will not be derived from the rain which falls on the area immediately surrounding its mouth, but from that which falls on the outcrop of the pervious stratum below the impervious one

just mentioned; and if this outcrop be in a district which is uninhabited and uncultivated, the water of the well will probably be entirely free from organic impurity or products of decomposition. But even if the water be polluted at its source, still it must pass through a very extensive filter before it reaches the well, and its organic matter will probably be in great measure converted by oxidation into bodies in themselves innocuous.

This is very briefly the general history of natural waters, and the problem presented to the analyst is to ascertain, as far as possible, from the nature and quantity of the impurities present, the previous history of the water, and its present condition and fitness for the purpose for which it is to be used.

It is impossible to give any fixed rule by which the results obtained by the foregoing method of analysis should be interpreted. The analyst must form an independent opinion for each sample from a consideration of all the results he has obtained. Nevertheless, the following remarks, illustrated by reference to the examples given in the accompanying table, which may be considered as fairly typical, will probably be of service. (See Table, pp. 474, 475).

Total Solid Matter.

Waters which leave a large residue on evaporation are, as a rule, less suited for general domestic purposes than those which contain less matter in solution, and are unfit for many manufacturing purposes. The amount of residue is also of primary importance as regards the use of the water for steam boilers, as the quantity of incrustation produced will chiefly depend upon it. It may vary considerably, apart from any unnatural pollution of the water, as it depends principally on the nature of the soil through or over which the water passes. River water, when but slightly polluted, contains generally from 10 to 40 parts. Shallow well water varies greatly, containing from 30 to 150 parts, or even more, as in examples X. and XIII., the proportion here depending less on the nature of the soil than on the original pollution of the water. Deep well water also varies considerably; it usually contains from 20 to 70 parts, but this range is frequently overstepped, the quantity depending largely upon the nature of the strata from which the water is obtained. Example XV. being in the New Red Sandstone, has a small proportion, but XVII. and XVIII. in the Chalk have a much larger quantity. Spring waters closely resemble those from deep wells. Sewage contains generally from 50 to 100 parts, but occasionally less, and frequently much more as in example XXXIV. The total solid matter, as a rule, exceeds the sum of the constituents determined; the nitrogen, as nitrates and nitrites, being calculated as potassium nitrate, and the chlorine as sodium chloride; but occasionally this is not the case, owing, it is likely, to the presence of some of the calcium as nitrate or chloride.

Organic Carbon or Nitrogen.

The existing condition of the sample, so far as organic contamination is concerned, must be inferred from the amount of these two constituents. In a good water, suitable for domestic supply, the former should not, under ordinary circumstances, exceed 0·2 and the latter 0·02 part.

Waters from districts containing much peat are often coloured more or less brown, and contain an unusual quantity of organic carbon, but this peaty matter is probably innocuous unless the quantity be extreme. The large proportion of organic carbon and nitrogen given in the average for unpolluted upland surface water in Table (XXVIII.) is chiefly due to the fact that upland gathering grounds are very frequently peaty. The examples given (I. to V.) may be taken as fairly representative of the character of upland surface waters free from any large amount of peaty matter. In surface waters from cultivated areas the quantity of organic carbon and nitrogen is greater, owing to increased density of population, the use of organic manures, etc., the proportion being about 0·25 to 0·3 part of organic carbon, and 0·04 to 0·05 part of organic nitrogen. The water from shallow wells varies so widely in its character that it is impossible to give any useful average. In many cases, as for example in XIII.

and XIV, the amount is comparatively small, although the original pollution, as shown by the total inorganic nitrogen and the chlorides, was very large; the organic matter in these cases having been almost entirely destroyed by powerful oxidation. In VIII. and IX. the original pollution was slight; and oxidation being active, the organic carbon and nitrogen have been reduced to extremely small quantities. On the other hand, in XI. the proportion of organic matter is enormous, the oxidizing action of the surrounding soil being utterly insufficient to deal with the pollution. The danger attending the use of shallow well waters, which contain when analyzed very small quantities of organic matter, arises chiefly from the liability of the conditions to variation. Change of weather and many other circumstances may at any time prevent the purification of the water, which at the time of the analysis appeared to be efficient. Moreover, it is by no means certain that an oxidizing action which would be sufficient to reduce the organic matter in a water to a very small proportion would be equally competent to remove the specific poison of disease. Hence the greater the impurity of the source of a water the greater the risk attending its use.

In deep well waters the quantity of organic carbon and nitrogen also extends through a wide range, but is generally low, the average being about 0·06 part carbon and 0·02 part nitrogen (XXIX.). Here the conditions are usually very constant, and if surface drainage be excluded, the source of the water is of less importance. Springs in this, as in most other respects, resemble deep wells; the water from them being generally, however, somewhat purer. In sewage great variations are met with. On the average it contains about four parts of organic carbon and two parts of organic nitrogen (XXXII. and XXXIII.), but the range is very great. In the table, XXXIV. is a very strong sample, and XXXV. a weak one. The effluent water from land irrigated with sewage is usually analogous to waters from shallow wells, and its quality varies greatly according to the character of the sewage and the conditions of the irrigation.

Ratio of Organic Carbon to Organic Nitrogen.

The ratio of the organic carbon to the organic nitrogen given in the seventh column of the table (which shows the fourth term of the proportion—organic nitrogen : organic carbon : : 1 : x), is of great importance as furnishing a valuable indication of the nature of the organic matter present. When this is of vegetable origin, the ratio is very high, and when of animal origin very low. This statement must, however, be qualified, on account of the different effect of oxidation on animal and vegetable substances. It is found that when organic matter of vegetable origin, with a high ratio of carbon to nitrogen, is oxidized, it loses carbon more rapidly than nitrogen, so that the ratio is reduced. Thus unoxidized peaty waters exhibit a ratio varying from about 8 to 20 or even more, the average being about 12; whereas, the ratio in spring water originally containing peaty matter, varies from about 2 to 5, the average being about 3·2. When the organic matter is of animal origin the action is reversed, the ratio being increased by oxidation. In unpolluted upland surface waters the ratio varies from about 6 to 12, but in peaty waters it may amount to 20 or more. In surface water from cultivated land it ranges from about 4 to 10, averaging about 6. In water from shallow wells it varies from about 2 to 8, with an average of about 4, but instances beyond this range in both directions are very frequent. In water from deep wells and springs, the ratio varies from about 2 to 6 with an average of 4, being low on account, probably, of the prolonged oxidation to which it has been subjected, which, as has been stated above, removes carbon more rapidly than nitrogen. In sea water this action reaches a maximum, the time being indefinitely prolonged, and the ratio is on the average about 1·7. This is probably complicated by the presence, in some cases, of multitudes of minute living organisms. In sewage the ratio ranges from about 1 to 3, with an average of about 2.

When, in the case of a water containing much nitrogen as nitrates and nitrites, this ratio is unusually low, incomplete destruction of nitrates during the evaporation may be suspected, and the determination should be repeated. To provide for this contingency, if a water contain any considerable quantity of

ammonia, it is well, when commencing the evaporation in the first instance, to set aside a quantity sufficient for this repetition, adding to it the usual proportion of sulphurous acid.

Nitrogen as Ammonia.

The ammonia in natural waters is derived almost exclusively from animal contamination, and its quantity varies between very wide limits. In upland surface waters it seldom exceeds 0·008 part, the average being about 0·002 part. In water from cultivated land the average is about 0·005, and the range is greater, being from *nil* to 0·025 part, or even more. In water from shallow wells the variation is so great that it would be useless to attempt to state an average, all proportions from *nil* to as much as 2·5 parts having been observed. In waters from deep wells a very considerable proportion is often found, amounting to 0·1 part or even more, the average being 0·01 part, and the variations considerable. In spring water it is seldom that more than 0·01 part of nitrogen as ammonia occurs, the average being only 0·001 part. Sewage usually contains from 2 to 6 parts, but occasionally as much as 9 or 10 parts, the average being about five. Ammonia is readily oxidized to nitrites and nitrates, and hence its presence, in considerable quantity, usually indicates the absence of oxidation, and is generally coincident with the presence of organic matter. That sometimes found in waters from very deep wells is, however, probably due to subsequent decomposition of nitrates.

Albuminoid Ammonia.

Wanklyn's standards for albuminoid ammonia are

High purity,	0·0 to 0·0041 parts per 100,000.
Satisfactory,	0·0041 to 0·0082 ,, ,,
Impure,	over 0·0082 ,, ,,

In the absence of free ammonia, he does not condemn a water unless the albuminoid exceeds ·0082, but a water yielding ·0123 he condemns in any circumstances. When the albuminoid ammonia process was introduced it was well known that there was a varying relation between the quantities of albuminoid ammonia and the amounts of different kinds of nitrogenous organic matter. The researches of numerous chemists have confirmed the inference that, although a useful indication, too much importance must not be attached to this figure.

Nitrogen as Nitrates and Nitrites.

Nitrates and nitrites are produced by the oxidation of nitrogenous organic matter, and almost always from animal matter. In upland surface waters the proportion varies from *nil* to 0·05 part or very rarely more, but the majority of samples contain none or mere traces (I. to V.), the average being about 0·009 part. In surface waters from cultivated land the quantity is much greater, varying from *nil*, which seldom occurs, to 1 part, the average being about 0·25 part. The proportion in shallow wells is usually much greater still, ranging from *nil*, which very rarely occurs, to as much as 25 parts, It would probably be useless to attempt to state an average, but quantities of from 2 to 5 parts occur most frequently. In water from deep wells the range is from *nil* to about 3 parts, and occasionally more, the average being about 0·5 part. In spring water the range is about the same as in deep well water, but the average is somewhat lower.

It sometimes happens that, when the supply of atmospheric oxygen is deficient, the organic matter in water is oxidized at the expense of the nitrates present; and occasionally, if the quantities happen to be suitably proportioned, they are mutually destroyed, leaving no evidence of pollution. This reduction of nitrates often occurs in deep well water, as for example, in that from wells in the Chalk beneath London Clay, where the nitrates are often totally destroyed. In sewages, putrefaction speedily sets in, and during this condition the nitrates

are rapidly destroyed, and so completely and uniformly that it is probably needless to attempt their determination, except in sewages which are very weak, or for other special reasons abnormal. Out of a large number of samples, only a very few have been found which contained any nitrates, and those only very small quantities.

Nitrites occurring in deep springs or wells no doubt arise from the deoxidation of nitrates by ferrous oxide, or certain forms of organic matter of a harmless nature; but whenever they occur in shallow wells or river water, they may be of much greater significance. Their presence in such cases is most probably due to recent sewage contamination, and such waters must be looked upon with great suspicion.

Total Inorganic Nitrogen.

When organic matter is oxidized it is ultimately resolved into inorganic substances. Its carbon appears as carbonic acid, its hydrogen as water, and its nitrogen as ammonia, nitrous acid, or nitric acid; the last two combining with the bases always present in water to form nitrites and nitrates. The carbon and hydrogen are thus clearly beyond the reach of the analyst; but the nitrogen compounds, as has been shown, can be accurately determined, and furnish us with a means of estimating the amount of organic matter which was formerly present in the water, but which has already undergone decomposition.

The sum of the amounts of nitrogen found in these three forms constitutes then a distinct and valuable term in the analysis, the *organic* nitrogen relating to the *present*, and the total *inorganic* nitrogen to the *past* conditions of the water. Since ammonia, nitrites, and nitrates are quite innocuous, the total inorganic nitrogen does not indicate *actual* evil like the organic nitrogen, but *potential* evil, as it is evident that the innocuous character of a water which contains much nitrogen in these forms depends wholly on the permanence of the conditions of temperature, aëration, filtration through soil, etc., which have broken up the original organic matter; it these should at any time fail, the *past* contamination would become *present*, the nitrogen appearing in the organic form, the water being loaded in all likelihood with putrescent and contagious matter.

In upland surface waters which have not been contaminated to any extent by animal pollution the total inorganic nitrogen rarely exceeds 0·03 part. In water from cultivated districts the amount is greater, ranging as high as 1 part, the average of a large number of samples being about 0·22 part. It is useless to attempt any generalization for shallow wells, as the proportion depends upon local circumstances. The amount is usually large and may reach, as seen in Examples XIII., the enormous quantity of twenty-five parts per 100,000. Waters containing one to five parts are very commonly met with. In water from deep wells and springs, quantities ranging up to 3·5 parts have been observed, the average on a large series of analyses being 0·5 part for deep wells, and about 0·4 part for springs. It must be remembered that the conditions attending deep wells and springs are remarkably permanent, and the amount of filtration which the water undergoes before reaching the well itself, or issuing from the spring is enormous. Meteorological changes here have either no effect, or one so small and slow as not to interfere with any purifying actions which may be taking place. All other sources of water, and especially shallow wells, are on the other hand subject to considerable changes. A sudden storm after drought will wash large quantities of polluting matter into the water-course; or dissolve the filth which has been concentrating in the pores of the soil during the dry season, and carry it into the well. Small indications therefore of a polluted origin are very serious in surface waters and shallow well waters, but are of less moment in water from deep wells and springs; the *present* character of these being of chief importance, since whatever degree of purification may be observed, may usually be treated as permanent. The term "total inorganic nitrogen" has been chosen chiefly because it is based on actual results of analysis without the introduction of any theory whatever. It will be seen that it corresponds very nearly with the term "previous sewage or animal contamination," which was introduced by Dr. Frankland, and which was employed in the second edition of this work. Perhaps few terms have been more woefully mis-

understood and misrepresented than that phrase, and it is hoped that the new term will be less liable to misconception. It will be remembered the "previous sewage contamination" of a water was calculated by multiplying the sum of the quantities of nitrogen present as ammonia, nitrates, and nitrites, by 10,000 and deducting 320 from the product, the number thus obtained representing the previous animal contamination of the water in terms of average filtered London sewage. In was purely conventional, for the proportion of organic nitrogen present is such sewage was assumed to be 10 parts per 100,000, whereas in the year 1857 it was actually 8·4 parts, and in 1869 only 7 parts. The deduction of 320 was made to correct for the average amount of inorganic nitrogen in rain water, and this is omitted in calculating "total inorganic nitrogen" for the following reasons:—The quantity is small, and the variations in composition of rain water at different times and under different circumstances very considerable, and it appears to obscure the significance of the results of analysis of very pure waters to deduct from all the same fixed amount. As, too, the average amount of total inorganic nitrogen in unpolluted surface waters is only 0·011 part (XXVIII.), it cannot be desirable to apply a correction amounting to nearly three times that average, and so place a water which contains 0·032 part of total inorganic nitrogen on the same level as one which contains no trace of any previous pollution.

Chlorine.

This is usually present as sodium chloride, but occasionally, as has been mentioned before, it is most likely as a calcium salt. It is derived, in some cases, from the soil, but more usually from animal excreta (human urine contains about 500 parts per 100,000), and is therefore of considerable importance in forming a judgment as to the character of a water. Unpolluted river and spring waters usually contain less than one part; average town sewage about eleven parts. Shallow well water may contain any quantity from a mere trace up to fifty parts or even more. Its amount is scarcely affected by any degree of filtration through soil: thus the effluent water from land irrigated with sewage contains the same proportion of chlorine as the sewage, unless it has been diluted by subsoil water or concentrated by evaporation. Of course, attention should be given to the geological nature of the district from which the water comes, the distance from the sea or other source of chlorine, etc., in order to decide on the origin of the chlorine. Under ordinary circumstance, a water containing more than three or four parts of chlorine should be regarded with suspicion.

Hardness.

This is chiefly of importance as regards the use of the water for cleansing and manufacturing purposes, and for steam boilers. It is still a moot point as to whether hard or soft water is better as an article of food. The temporary hardness is often said to be that due to carbonates held in solution by carbonic acid, but this is not quite correct; for even after prolonged boiling, water will still retain about three parts of carbonate in solution, and therefore when the total hardness exceeds three parts, that amount should be deducted from the permanent hardness and added to the temporary, in order to get the quantity of carbonate in solution. But the term "temporary" hardness properly applies to the amount of hardness which may be removed by boiling, and hence, if the total hardness be less than three parts, there is usually no *temporary*. As the hardness depends chiefly on the nature of the soil through and over which the water passes, the variations in it are very great; that from igneous strata has least hardness, followed in approximate order by that from Metamorphic, Cambrian, Silurian and Devonian rocks, Millstone Grit, London Clay, Bagshot Beds, New Red Sandstone, Coal Measures, Mountain Limestone, Oolite, Chalk, Lias, and Dolomite, the average in the case of the first being 2·4 parts, and of the last 41 parts. As animal excreta contain a considerable quantity of lime, highly polluted waters are usually extremely hard. Water from shallow wells contains varying proportions up to nearly 200 parts

of total hardness (XIII.). No generalization can be made as to the proportion of permanent to temporary hardness.

Suspended Matter.

This is of a less degree of importance than the matters hitherto considered. From a sanitary point of view it is of minor interest, because it may be in most cases readily and completely removed by filtration. Mineral suspended matter is, however, of considerable mechanical importance as regards the formation of impediments in the river bed by its gradual deposition, and as regards the choking of the sand filters in water-works; and organic suspended matter is at times positively injurious, and always favours the growth of minute organisms.

From the determinations which have been described, it is believed that a sound judgment as to the character of a water may be made, and the analyst should hardly be content with a less complete examination. If, however, from lack of time or other cause, so much cannot be done, a tolerably safe opinion may be formed, omitting the determination of total solid matter, and organic carbon and nitrogen. But it must not be forgotten that by so doing the inquiry is limited, as regards organic impurity, to the determination of that which was formerly present, but has already been converted into inorganic substances. If still less must suffice, the determination of nitrogen as nitrates and nitrites may be omitted, its place being to a certain extent supplied by that of chlorine, but especial care must then be taken to ascertain the source of the latter by examination of the district. If it be in any degree of mineral origin, no opinion can be formed from it as to the likelihood of organic pollution.

General Considerations.

In judging of the character of a sample of water, due attention must of course be paid to the purpose for which it is proposed to be used. The analyst frequently has only to decide broadly whether the water is good or bad; as, for example, in cases of the domestic supply to isolated houses or of existing town supplies. Water which would be fairly well suited for the former might be very objectionable for the latter, where it would be required to a certain extent for manufacturing purposes. Water which would be dangerous for drinking or cooking may be used for certain kinds of cleansing operations; but it must not be forgotten, that unless great care and watchfulness are exercised there is considerable danger of this restriction being neglected, and especially if the objectionable water is nearer at hand than the purer supply. There would for this reason, probably, be some danger attending a double supply on a large scale in a town, even if the cost of a double service of mains, etc., were not prohibitive.

It is often required to decide between several proposed sources of supply, and here great care is necessary, especially if the differences between the samples are not great. If possible, samples should be examined at various seasons of the year; and care should be taken that the samples of the several waters are collected as nearly as possible simultaneously and in a normal condition. The general character of a water is most satisfactorily shown by the average of a systematic series of analyses; and for this reason the average analysis of the water supplies of London, taken from the Reports of Dr. Frankland to the Registrar General, of Glasgow by Dr. Mills, and of Birmingham by Dr. Hill, are included in the table. River waters should, as a rule, not be examined immediately after a heavy rain when they are in flood. A sudden rainfall after a dry season will often foul a river more than a much heavier and more prolonged downfall after average weather. Similarly the sewage discharged from a town at the beginning of a heavy rainstorm is usually extremely foul, the solid matter which has been accumulating on the sides of the sewers, and in corners and recesses, being rapidly washed out by the increased stream.

The possibility of *improvement* in quality must also be considered. A turbid water may generally be rendered clear by filtration, and this will often also effect some slight reduction in the quantity of organic matter; but while somewhat rapid filtration through sand or similar material will usually remove

all solid suspended matter, it is generally necessary to pass the water very slowly through a more efficient material to destroy any large proportion of the organic matter in solution. Very fine sand, animal charcoal, and spongy iron are all in use for this purpose. The quantity of available oxygen must not be neglected in considering the question of filtration. If the water contains only a small quantity of organic matter and is well aërated, the quantity of oxygen in solution may be sufficient, and the filtration may then be continuous; but in many instances this is not the case, and it is then necessary that the filtration should be intermittent, the water being allowed at intervals to drain off from the filtering material in order that the latter may be well aërated, after which it is again fit for work.

Softening water by Clark's process generally removes a large quantity of organic matter (see Table, XVI.) from solution, it being carried down with the calcium carbonate precipitate.

It is evident that no very definite distinction can be drawn between deep and shallow wells. In the foregoing pages, deep wells generally mean such as are more than 100 feet deep, but there are many considerations which qualify this definition. A deep well may be considered essentially as one the water in which has filtered through a considerable thickness of porous material, and whether the shaft of such a well is deep or shallow will depend on circumstances. If the shaft passes through a bed of clay or other impervious stratum, and the surface water above that is rigidly excluded, the well should be classed as "deep," even if the shaft is only a few feet in depth, because the water in it must have passed for a considerable distance below the clay. On the other hand, however deep the shaft of a well, it must be considered as "shallow" if water can enter the shaft near the surface, or if large cracks or fissures give free passage for surface water through the soil in which the well is sunk. With these principles in view, the water from wells may often be improved. Every care should be taken to exclude surface water from deep wells; that is to say, all water from strata within about 100 feet from the surface or above the first impervious bed. In very deep wells which pass through several such beds, it is desirable to examine the water from each group of pervious strata, as this often varies in quality, and if the supply is sufficient, exclude all but the best.

In shallow wells much may occasionally be accomplished in a similar manner by making the upper part of the shaft water-tight. It is also desirable that the surface for some distance round the well should be puddled with clay, concreted, or otherwise rendered impervious, so as to increase the thickness of the soil through which the water has to pass. Drains passing near the well should be, if possible, diverted; and of course cesspools should be either abolished, or, if that is impracticable, removed to as great a distance from the well as is possible, and in addition made perfectly water-tight. Changes such as these tend to diminish the uncertainty of the conditions attending a shallow well, but in most cases such a source of supply should, if possible, be abandoned as dangerous at best.

PART VII.

VOLUMETRIC ANALYSIS OF GASES.

Description of the necessary Apparatus, with Instructions for Preparing, Etching, Graduating, etc.

THIS branch of chemical analysis, on account of its extreme accuracy, and in consequence of the possibility of its application to the analysis of carbonates, and of many other bodies from which gases may be obtained, deserves more attention than it has generally received, in this country at least. It will therefore be advisable to devote some considerable space to the consideration of the subject.

For an historical sketch of the progress of gas analysis, the reader is referred to Dr. Frankland's article in the *Handwörterbuch der Chemie*, and more complete details of the process than it will be necessary to give here will be found in that article; also in Bunsen's *Gasometry* and in Dr. Russell's contributions to Watts's *Dictionary of Chemistry*.

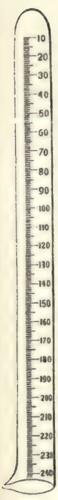


Fig. 70.

The apparatus employed by Bunsen, who was the first successfully to work out the processes of gas analysis, is very simple. Two tubes, the absorption tube and the eudiometer, are used, in which the measurement and analysis of the gases are performed. The first of these tubes is about 250 mm. long and 20 mm. in diameter, closed at one end, and with a lip at one side of the open extremity, to facilitate the transference of the gas from the absorption tube (fig. 70) to the eudiometer (fig. 71). The eudiometer has a length of from 700 to 800 mm., and a diameter of 20 mm. Into the closed end two platinum wires are sealed, so as to enable the operator to pass an electric spark through any gas which the tube may contain. The mode of sealing in the platinum wires is as follows:—When the end of the tube is closed, and while still hot, a finely pointed blowpipe flame is directed against the side of the tube at the base of the hemispherical end. When the glass is soft, a piece of white-hot platinum wire is pressed against it and rapidly drawn away. By this means a small conical tube is produced. This operation is then repeated on the opposite side (fig. 72). One of the conical tubes is next cut off near to the eudiometer, so as to leave a small orifice (fig. 73), through which a piece of the moderately thin platinum wire, reaching about two-thirds across the tube, is passed. The fine blowpipe flame is now brought to play on the wire at the point where it enters the tube; the glass rapidly fuses round the wire, making a perfectly gas-tight joint. If it should be observed that the tube has any tendency to collapse during the heating, it will be necessary

to blow gently into the open end of the tube. This may be conveniently done by means of a long piece of caoutchouc connector, attached to the eudiometer, which enables the operator to watch the effect of the blowing more easily than if the mouth were applied directly to the tube. When a perfect fusion of the glass round the wire has been effected, the point on the opposite side is cut off, and a second wire sealed in in the same manner (fig. 74). The end of the tube must be allowed to cool very slowly; if proper attention is not paid to this, fracture is very liable to ensue. When perfectly cold, a piece of wood with a rounded end is passed up the eudiometer, and the two wires carefully pressed against the end of the tube, so as to lie in contact with the glass, with a space of 1 or 2 mm. between their points (fig. 75). It is for this purpose that the wires, when sealed in, are made to reach so far across the tube. The ends of the wires projecting outside the tube are then bent into loops. These loops must be carefully treated, for if frequently bent they are very apt to break off close to the glass; besides this, the bending of the wire sometimes causes a minute crack in the glass, which may spread and endanger the safety of the tube. These difficulties may be overcome by cutting off the wire close to the glass, and carefully smoothing the ends by rubbing them with a piece of ground glass until they are level with the surface of the tube (fig. 76). In order to make contact with the induction coil, a wooden American paper-clip, lined with platinum foil, is made to grasp the tube; the foil is connected with two strong loops of platinum wires, and to these the wires from the coil are attached (fig. 77). In this way no strain is put on the eudiometer wires by the weight of the wires from the coil, and perfect contact is ensured between the foil and platinum wires. It is also easy to clean the outside of the eudiometer without fear of injuring the instrument.

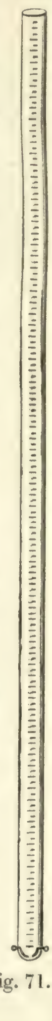


Fig. 71.

It will now be necessary to examine if the glass is perfectly fused to the wires. For this purpose the eudiometer is filled with mercury, and inverted in the trough. If the tube has 800 mm. divisions, a vacuous space will be formed in the upper end. Note the height of the mercury, and if this remains constant for a while the wires are properly sealed. Should the eudiometer be short, hold it in the hands, and bring it down with a quick movement upon the edge of the india-rubber cushion at the bottom of the trough, taking care that the force of impact is slight, else the mercury may fracture the sealed end of the tube. By jerking the eudiometer thus, a momentary vacuum is formed, and if there is any leakage, small bubbles of air will arise from the junction of the wires with the glass.

The tubes are graduated by the following processes:—A cork is fitted into the end of the tube, and a piece of stick, a file, or any-

thing that will make a convenient handle, is thrust into the cork. The tube is heated over a charcoal fire or combustion furnace, and coated with melted wax by means of a camel's-hair brush. Sometimes a few drops of turpentine are mixed with the wax to render it less brittle, but this is not always necessary. If on cooling it should be found that the layer of wax is not uniform, the tube may be placed in a perpendicular position before a fire and slowly rotated so as to heat it evenly. The wax will then be evenly distributed on the surface of the glass, the excess flowing off. The

Fig. 72.

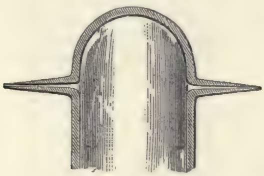
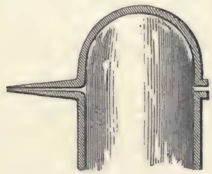


Fig. 73.



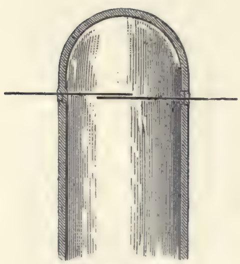


Fig. 74.

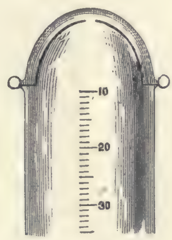


Fig. 75.

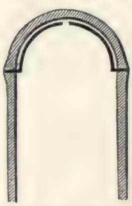


Fig. 76.

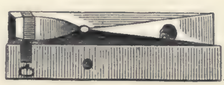


Fig. 77.

tube must not be raised to too high a temperature, or the wax may become too thin; but all thick masses should be avoided, as they may prove troublesome in the subsequent operation.

The best and most accurate mode of marking the millimetre divisions on the wax is by a graduating machine; but the more usual process is to copy the graduations from another tube in the following manner. A hard glass tube, on which millimetre divisions have already been deeply etched, is fixed in a groove in the graduating table, a straight-edge of brass being screwed down on the tube

and covering the ends of the lines. The standard tube is shown in the figure at the right-hand end of the apparatus (fig. 78). The waxed tube is secured at the other end of the same groove, and above it are fixed two brass plates, one with a straight-edge, and the other with notches at intervals of 5 mm. the alternate notches being longer than the intermediate ones (fig. 79). A stout rod of wood provided with a sharp steel point near one end, and a penknife blade at the other (fig. 80), is held so that the steel point rests in one of the divisions of the graduated tube, being gently pressed at the same time against the edge of the brass plate; the point of the knife-blade is then moved by the operator's right hand across the portion of the waxed tube which lies exposed between the two brass plates. When the line has been scratched on the wax, the point is moved along the tube until it falls into the next division; another line is now scratched on the wax, and so on. At every fifth division the knife-blade will enter the notches in the brass plate, making a longer line on the tube. After a little practice it will be found easy to do fifty or sixty divisions in a minute, and with perfect regularity. Before the tube is removed from the apparatus, it must be carefully examined to see if any mistake has been made. It may have happened that during the graduation the steel point slipped out of one of the divisions in the standard tube; if this has taken place, it will be found that the distance between the line made at that time and those on each side of it will not be equal, or a crooked or double line may have been produced. This is easily obliterated by touching the wax with a piece of heated

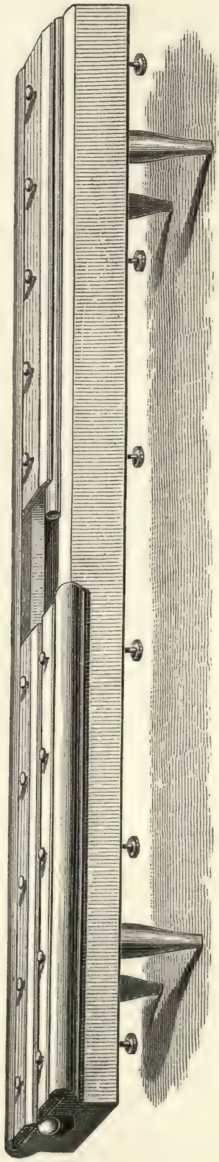


Fig. 78.

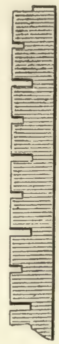


Fig. 79.


Fig. 80.

platinum wire, after which another line is marked. The tube is now taken out of the table, and once more examined. If any portions of wax have been scraped off by the edges of the apparatus, or by the screws, the coating must be repaired with the hot platinum wire. Numbers have next to be marked opposite each tenth division, beginning from the closed end of the tube, the first division, which should be about 10 mm. from the end, being marked 10 (see fig. 75). The figures may be well made with a steel pen.

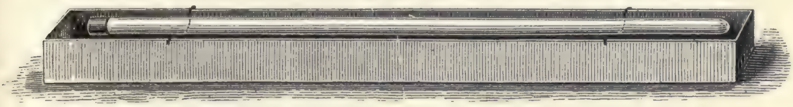


Fig. 81.

This has the advantage of producing a double line when the nib is pressed against the tube in making a down stroke. The date, the name of the maker of the tube, or its number, may now be written on the tube.

The etching by gaseous hydrofluoric acid is performed by supporting the tube by two pieces of wire over a long narrow leaden trough containing sulphuric acid and powdered fluor-spar (fig. 81), and the whole covered with a cloth or sheet of paper. Of course it is necessary to leave the cork in the end of the tube to prevent the

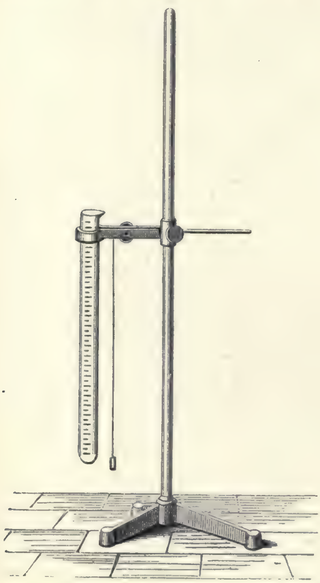


Fig. 82.

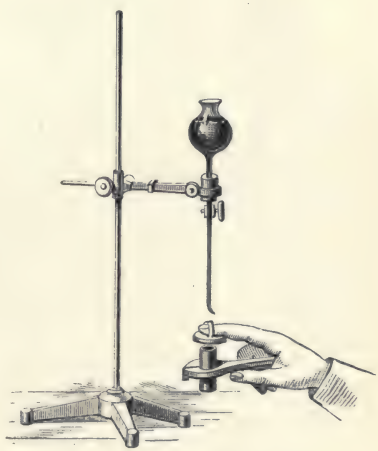


Fig. 83.

access of hydrofluoric acid to the interior, which might cause the tube to lose its transparency to a considerable extent. The time

required for the action of the gas varies with the kind of glass employed. With ordinary flint glass from ten minutes to half an hour is quite sufficient; if the leaden trough is heated, the action will take place still more rapidly. The tube is removed from time to time, and a small portion of the wax scraped off from a part of one of the lines; and if the division can be felt with the finger-nail or the point of a knife, the operation is finished; if not, the wax must be replaced, and the tube restored to the trough. When sufficiently etched, the tube is washed with water, heated before a fire, and the wax wiped off with a warm cloth.

The etching may also be effected with liquid hydrofluoric acid, by applying it to the divisions on the waxed tube with a brush, or by placing the eudiometer in a gutta-percha tube closed at one end, and containing some of the liquid.

As all glass tubes are liable to certain irregularities of diameter, it follows that equal lengths of a graduated glass tube will not contain exactly equal volumes; hence it is, of course, impossible to obtain by measurement of length the capacity of the closed end of the tube.

In order to provide for this, the tube must be carefully calibrated. For this purpose it is supported vertically (fig. 82), and successive quantities of mercury poured in from a measure. This measure should contain about as much mercury as ten or twenty divisions of the eudiometer, and is made of a piece of thick glass tube, closed at one end, and with the edges of the open end ground perfectly flat. The tube is fixed into a piece of wood in order to avoid heating its contents during the manipulation. The measure may be filled with mercury from a vessel closed with a stop-cock terminating in a narrow vertical tube, which is passed to the bottom of the measure (fig. 83). On carefully opening the stop-cock the mercury flows into the measure without leaving any air-bubbles adhering to the sides. A glass plate is now pressed on the ground edges of the tube, which expels the excess of mercury and leaves the measure entirely filled. The mercury may be introduced into the measure in a manner which is simpler and as effectual, though perhaps not quite so convenient, by first closing it with a glass plate, and depressing it in the mercurial trough, removing the plate from the tube, and again replacing it before raising the measure above the surface of the mercury. After pouring each measured quantity of mercury into the eudiometer, the air-bubbles are carefully detached from the sides by means of a thin wooden rod or piece of whalebone, and the level of the mercury at the highest part of the curved surface observed.

In all measurements in gas analysis it is, of course, essential that the eye should be exactly on a level with the surface of the mercury, for the parallax ensuing if this were not the case would produce grave errors in the readings. The placing of the eye in the proper position may be ensured in two ways. A small piece of looking-glass (the back of which is painted, or covered with paper to prevent

the accidental soiling of the mercury in the trough) is placed behind, and in contact with the eudiometer. The head is now placed in such a position that the reflection of the pupil of the eye is precisely on a level with the surface of the mercury in the tube and the measurement made. As this process necessitates the hand of the operator being placed near the eudiometer, which might cause the warming of the tube, it is preferable to read off with a telescope placed at a distance of from two to six feet from the eudiometer. The telescope is fixed on a stand in a horizontal position, and the support is made to slide on a vertical rod. The image of the surface of the mercury is brought to the centre of the field of the telescope, indicated by the cross wires in the eyepiece, and the reading taken. The telescope has the advantage of magnifying the graduations, and thus facilitating the estimation by the eye of tenths of the divisions. Fig. 84 represents the appearance of the tube and mercury as seen by an inverting telescope.

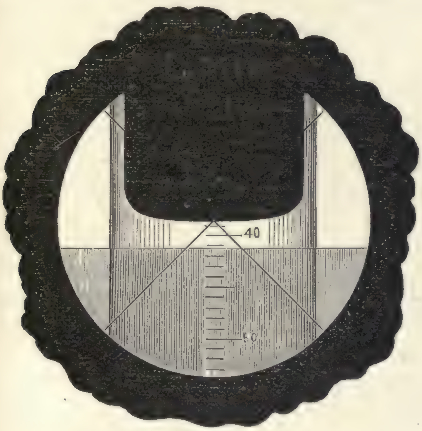


Fig. 84.

By this method the capacity of the tube at different parts of its length is determined. If the tube were of uniform bore, each measure of mercury would occupy the same length in the tube ; but as this is never the case, the value of the divisions at all parts of the tube will not be found to be the same.

From the data obtained by measuring the space in the tube which is occupied by equal volumes of mercury, a table is constructed by which the comparative values of each millimetre of the tube can be found. The following results were obtained in the calibration of a short absorption eudiometer :

On the introduction	of the	3rd	volume of mercury,	the reading was	12·8 mm.
,,	,,	,,	4th	,,	,,	18·4
,,	,,	,,	5th	,,	,,	24·0
,,	,,	,,	6th	,,	,,	29·8
,,	,,	,,	7th	,,	,,	35·2
,,	,,	,,	8th	,,	,,	41 0

Thus, the standard	volumes	occupied	5·6 mm.	between	12·8	and 18·4
,,	,,	,,	5·6	,,	18·4	,, 24·0
,,	,,	,,	5·8	,,	24·0	,, 29·8
,,	,,	,,	5·4	,,	29·8	,, 35·2
,,	,,	,,	5·8	,,	35·2	,, 41·0

If we assume the measure of mercury to contain 5·8 volumes (the greatest difference between two consecutive readings on the tube), the volume at the six points above given will be as follows :—

At 12·8 it will be 17·4 or 5·8 × 3
18·4 ,, 23·2 ,, 5·8 × 4
24·0 ,, 29·0 ,, 5·8 × 5
29·8 ,, 34·8 ,, 5·8 × 6
35·2 ,, 40·6 ,, 5·8 × 7
41·0 ,, 46·4 ,, 5·8 × 8

Between the first and second readings these 5·8 volumes are contained in 5·6 divisions, consequently each millimetre corresponds to $\frac{5{\cdot}8}{5{\cdot}6} = 1{\cdot}0357$ vol. This is also the value of the divisions between the second and third readings. Between the third and fourth 1 mm. contains 1 vol.; between the fourth and fifth, 1 mm. contains $\frac{5{\cdot}8}{5{\cdot}4} = 1{\cdot}0741$ vol.; and between the fifth and sixth mm. = 1 vol.

From these data the value of each millimetre on the tube can readily be calculated. Thus 13 will contain the value of 12·8 + the value of 0·2 of a division at this part of the tube, or 17·4 + (1·0357 × 0·2) = 17·60714. There is, however, no need to go beyond the second place of decimals, and, for all practical purposes, the first place is sufficient. Thus, by adding or subtracting the necessary volumes from the experimental numbers, we find the values of the divisions nearest to the six points at which the readings were taken to be—

13 = 17·61 or 17·6
18 = 22·79 ,, 22·8
24 = 29·00 ,, 29·0
30 = 35·00 ,, 35·0
35 = 40·38 ,, 40·4
41 = 46·40 ,, 46·4

In a precisely similar manner the values of the intermediate divisions are calculated, and we thus obtain the following table :—

Readings.	Values.		Readings.	Values.		Readings.	Values.	
10	14·50	14·5	21	25·89	25·9	32	37·15	37·1
11	15·54	15·5	22	26·93	26·9	33	38·22	38·2
12	16·57	16·6	23	27·96	28·0	34	39·30	39·3
13	17·61	17·6	24	29·00	29·0	35	40·38	40·4
14	18·65	18·6	25	30·00	30·0	36	41·40	41·4
15	19·68	19·7	26	31·00	31·0	37	42·40	42·4
16	20·71	20·7	27	32·00	32·0	38	43·40	43·4
17	21·75	21·8	28	33·00	33·0	39	44·40	44·4
18	22·79	22·8	29	34·00	34·0	40	45·40	45·4
19	23·82	23·8	30	35·00	35·0	41	46·40	46·4
20	24·86	24·9	31	36·07	36·1	&c.	&c.	&c.

If it be desired to obtain the capacity of the tube in cubic centimetres it is only necessary to determine the weight of the quantity of mercury the measure delivers, and the temperature at which the calibration was made, and to calculate the contents by the following formula :—

$$C = \frac{g \times (1 + 0{\cdot}0001815t)}{13{\cdot}596V}$$

in which g represents the weight of the mercury contained in the measure, t the temperature at which the calibration is made, 0·0001815 being the coefficient of expansion of mercury for each degree centigrade, V the volume read off in the eudiometer, and C the number of cubic centimetres required. (13·596 = sp. gr. of mercury at 0° C.)

A correction has to be made to every number in the table on account of the surface of the mercury assuming a convex form in the tube. During the calibration, the convexity of the mercury is turned towards the open end of the tube (fig. 85), whilst in the measurement of a gas the convexity will be in the opposite direction (fig. 86). It is obvious that the quantity of mercury measured during the calibration, while the eudiometer is inverted, will be less than a volume of gas contained in the tube when the mercury stands at the same division, while the eudiometer is erect. The necessary amount of correction is determined by observing the position of the top of the meniscus, and then introducing a few drops of a solution of corrosive sublimate, which will immediately cause the surface of the mercury to become horizontal (fig. 87), and again measuring.

It will be observed that in fig. 85 the top of the meniscus was at the division 39, whereas in fig. 87, after the addition of corrosive sublimate, the horizontal surface of the mercury stands at 38·7, giving a depression of 0·3 mm. If the tube were now placed vertical, and gas introduced so that the top of the meniscus was at

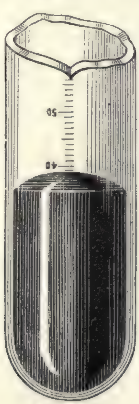


*Fig. 85.

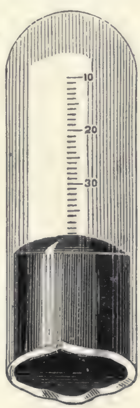


*Fig. 86.

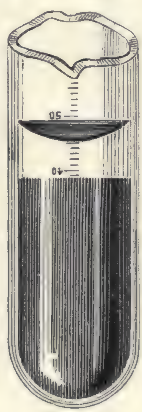


Fig. 87.

* In these the mercury should just touch 39.

39, and if it were now possible to overcome the capillarity, the horizontal surface would stand at 39·3. The small cylinder of gas between 38·7 and 39·3, or 0·6 division, would thus escape measurement. This number 0·6 is therefore called the *error of meniscus*, and must be added to all readings of gas in the eudiometer. The difference, therefore, between the two readings is multiplied by two, and the volume represented by the product obtained—the *error of meniscus*—is added to the measurements before finding the corresponding capacities by the table. In the case of the tube, of which the calibration is given above, the difference between the two readings was 0·4 mm., making the error of meniscus 0·8.

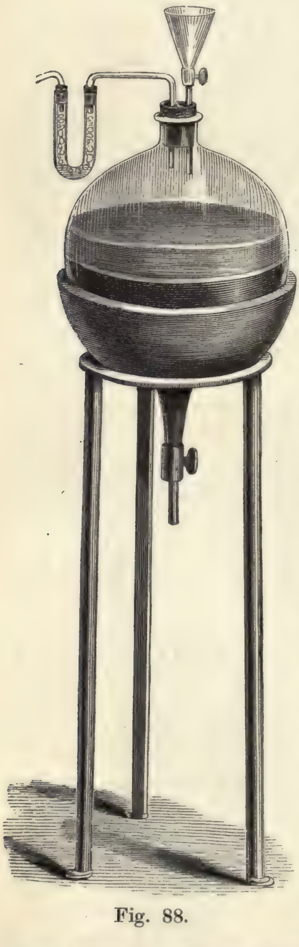


Fig. 88.

All experiments in gas analysis, with the apparatus described, should be conducted in a room set apart for the purpose, with the window facing the north, so that the sun's rays cannot penetrate into it, and carefully protected from flues or any source of heat which might cause a change of temperature of the atmosphere. The mercury employed should be purified, as far as possible, from lead and tin, which may be done by leaving it in contact with dilute nitric acid in a shallow vessel for some time, or by keeping it when out of use under concentrated sulphuric acid, to which some mercurous sulphate has been added. This mercury reservoir may conveniently be made of a glass globe with a neck at the top and a stop-cock at the bottom (fig. 88), which is not filled more than one-half, so as to maintain as large a surface as possible in contact with the sulphuric acid. Any foreign metals (with the exception of silver, gold, and platinum) which may be present are removed by the mercurous sulphate, an equivalent quantity of mercury being precipitated. This process, which was originated by M. Deville, has been in use for many years with very satisfactory results, the mercury being always clean and dry when drawn from the stop-cock at the bottom of the globe. The mouth of the globe should be kept closed to prevent the absorption of water by the sulphuric acid.

In all cases where practicable, gases should be measured when

completely saturated with aqueous vapour: to ensure this, the top of the eudiometer and absorption tubes should be moistened before the introduction of the mercury. This may be done by dipping the end of a piece of iron wire into water, and touching the interior of the closed extremity of the tube with the point of the wire.

In filling the eudiometer, the greatest care must of course be taken to exclude all air-bubbles from the tubes. This may be effected in several ways: the eudiometer may be held in an inverted or inclined position, and the mercury introduced through a narrow glass tube which passes to the end of the eudiometer and communicates, with the intervention of a stop-cock, with a reservoir of mercury (fig. 89). On carefully opening the stop-cock, the mercury slowly flows into the eudiometer, entirely displacing the air. The same result may be obtained by placing the eudiometer nearly in a horizontal position, and carefully introducing the mercury from a test tube without a rim (fig. 90). Any minute bubbles adhering to the side may generally be removed by closing the mouth of the tube with the thumb, and allowing a small air bubble to rise in the tube, and thus to wash it out. After filling the eudiometer entirely with mercury, and inverting it over a trough, it will generally be found that the air-bubbles have been removed.

For the introduction of the gases, the eudiometer should be placed in a slightly inclined position, being held by a support attached to

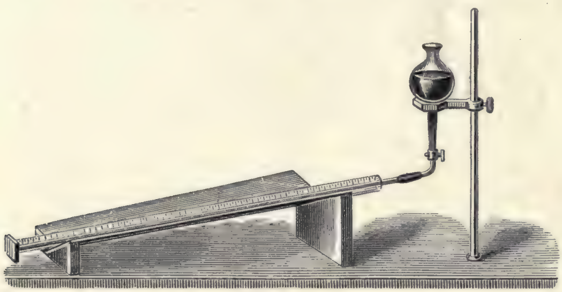


Fig. 89.

the mercurial trough (fig. 91), and the gas transferred from the tube in which it has been collected. The eudiometer is now put in an absolutely vertical position, determined by a plumb-line placed near it, and a thermometer suspended in close proximity. It must then be left for at least half an hour, no one being allowed to enter the room in the meantime. After the expiration of this period, the operator enters the room, and, by means of the telescope placed several feet from the mercury table, carefully observes the height of the mercury in the tube, estimating the tenths of a division with the eye, which can readily be done after a little practice. He next reads the thermometer with the telescope, and finally the height of the mercury in the trough is read off on the tube, for which purpose

the trough must have glass sides. The difference between these two numbers is the length of the column of mercury in the eudiometer, and has to be subtracted from the reading of the barometer. It only remains to take the height of the barometer. The most convenient form of instrument for gas analysis is the siphon barometer, with the divisions etched on the tube. This is placed on the mercury table, so that it may be read by the telescope immediately after the measurements in the eudiometer. There are two methods of numbering the divisions on the barometer: in one the zero point is at or near the bend of the tube, in which case the height of the lower column must be subtracted from that of the higher; in the other the zero is placed near the middle of the tube, so that the numbers have to be added to obtain the actual height. In cases of extreme accuracy, a correction must be made for the

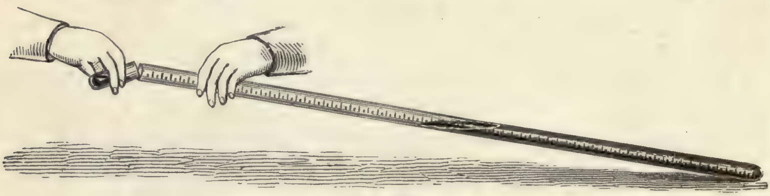


Fig. 90.

temperature of the barometer, which is determined by a thermometer suspended in the open limb of the instrument, and passing through a plug of cotton wool. Just before observing the height of the barometer, the bulb of the thermometer is depressed for a moment into the mercury in the open limb, thus causing a movement of the mercurial column, which overcomes any tendency that it may have to adhere to the glass.

In every case the volume observed must be reduced to the normal temperature and pressure, in order to render the results comparable. If the absolute volume is required, the normal pressure of 760 mm. must be employed; but when comparative volumes only are desired, the pressure of 1000 mm. is generally adopted, as it somewhat simplifies the calculation. In the following formula for correction of the volume of gases—

V_1 = the corrected volume.

V = the volume found in the table, and corresponding to the observed height of the mercury in the eudiometer, the error of meniscus being of course included.

B = the height of the barometer (corrected for temperature, if necessary) at the time of measurement.

b = the difference between the height of the mercury in the trough and in the eudiometer.

t = the temperature in centigrade degrees.

T = the tension of aqueous vapour in millimetres of mercury at $t°$. This number is, of course, only employed when the gas is saturated with moisture at the time of measurement.

Then

$$V_1 = \frac{V \times (B - b - T)}{760 \times (1 + 0{\cdot}003665t)}$$

when the pressure of 760 mm. is taken as the normal one; or,

$$V_1 = \frac{V \times (B - b - T)}{1000 \times (1 + 0{\cdot}003665t)}$$

when the normal pressure of 1 metre is adopted.

In cases where the temperature at measurement is below 0° (which rarely happens), the factor $1 - 0{\cdot}003665t$ must be used.

The following table may be of value in gas analysis :—

Density and volume of Mercury and of Water.

t°C.	Mercury.		Water.	
	Weight of 1 c.c.	Volume of 1 gm.	Weight of 1 c.c.	Volume of 1 gm.
0	13·596	·073551	·999884	1·000116
4	13·586	·073605	1·000013	·999987
5	13·584	·073617	1·000003	·999997
10	13·572	·073681	·999760	1·000240
15	13·559	·073752	·999173	1·000828
20	13·547	·073817	·998272	1·001731
25	13·535	·073885	·997133	1·002875
30	13·523	·073953	·995778	1·004240

Tables have been constructed containing the values of T; of $1000 \times (1 + 0{\cdot}003665t)$, and of $760 \times (1 + 0{\cdot}003665t)$, which very

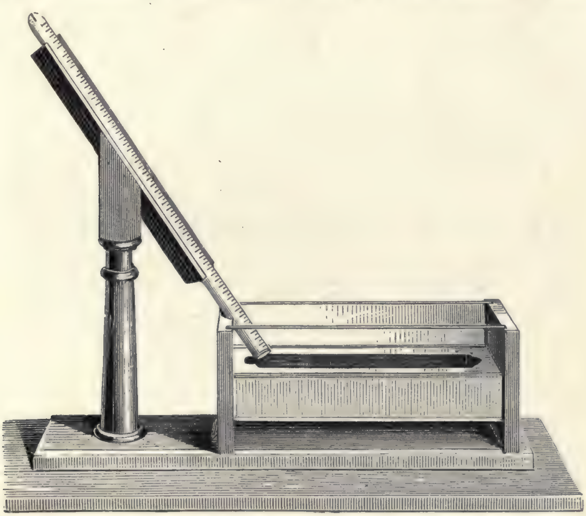


Fig. 91.

much facilitate the numerous calculations required in this branch of analysis.* These will be found at the end of the book.

We shall now be in a position to examine the methods employed in gas analysis. Some gases may be determined directly; that is, they may be absorbed by certain reagents, the diminution of the volume indicating the quantity of the gas present. Some are determined indirectly; that is, by exploding them with other gases, and measuring the quantities of the products. Some gases may be determined either directly or indirectly, according to the circumstances under which they are found.

1. GASES DETERMINED DIRECTLY.

A. Gases Absorbed by Crystallized Sodium Phosphate and by Potassium Hydrate :—

Hydrochloric acid, HCl,
Hydrobromic acid, HBr,
Hydriodic acid, HI.

B. Gases Absorbed by Potassium Hydrate, but not by Crystallized Sodium Phosphate :—

Carbonic anhydride, CO_2,
Sulphurous anhydride, SO_2,
Hydrosulphuric acid, H_2S.

C. Gases Absorbed by neither Crystallized Sodium Phosphate nor Potassium Hydrate :—

Oxygen, O_2,
Nitric oxide, NO,
Carbonic oxide, CO,
Hydrocarbons of the composition C_nH_{2n},
Hydrocarbons of the formula $(C_nH_{2n+1})_2$,
Hydrocarbons of the formula C_nH_{2n+2},
except Marsh gas.

2. GASES DETERMINED INDIRECTLY.

Hydrogen, H_2,
Carbonic oxide, CO,
Marsh gas, or Methane, CH_4,
Ethane, C_2H_6,
Ethyl hydride, C_2H_6,
Butane, C_4H_{10},
Propyl hydride, C_3H_8,
Butyl hydride, C_4H_{10},
Nitrogen, N_2.

* Mr. Sutton will forward a copy of these Tables, printed separately for laboratory use, to any one desiring them, on receipt of the necessary address.

DIRECT DETERMINATIONS.

Group A, consisting of Hydrochloric, Hydrobromic, and Hydriodic Acids.

In Bunsen's method the reagents for absorption are generally used in the solid form, in the shape of bullets. To make the bullets of sodium phosphate, the end of a piece of platinum wire, of about one foot in length, is coiled up and fixed in the centre of a pistol-bullet mould. It is well to bend the handles of the mould, so that when it is closed the handles are in contact, and may be fastened together by a piece of copper wire (fig. 92). The usual practice

Fig. 92.

Fig. 93.

is to place the platinum wire in the hole through which the mould is filled; but it is more convenient to file a small notch in one of the faces of the open mould, and place the wire in the notch before the mould is closed. In this manner the wire is not in the way during the casting, and it is subsequently more easy to trim the bullet. Some ordinary crystallized sodium phosphate is fused in a platinum crucible (or better, in a small piece of wide glass tube, closed at one end and with a spout at the other, and held by a copper-wire handle), and poured into the bullet mould (fig. 93). When quite cold, the mould is first gently warmed in a gas-flame, opened, and the bullet removed. If the warming of the mould is omitted, the bullet is frequently broken in consequence of its adhering to the metal. Some chemists recommend the use of sodium sulphate instead of phosphate, which may be made into balls by dipping the coiled end of a piece of platinum wire into the salt fused in its water of crystallization. On removing the wire, a small quantity of the salt will remain attached to the wire. When this has solidified, it is again introduced for a moment, and a larger quantity will collect; and this is repeated until the ball is sufficiently large. The balls must be quite smooth, in order to prevent the introduction of any air into the eudiometer. When the bullets are made in a mould, it is necessary to remove the short cylinder which is produced by the orifice through which the fused salt has been poured.

In the determination of these gases, it is necessary that they should be perfectly dry. This may be attained by introducing a bullet of

fused calcium chloride. After the lapse of about an hour, the bullet may be removed, the absorption tube placed in a vertical position, with thermometer, etc., arranged for the reading, and left for half an hour to acquire the temperature of the air. When the reading has been taken, one of the bullets of sodium phosphate or sodium sulphate is depressed in the trough, wiped with the fingers while under the mercury in order to remove any air that it might have carried down with it, and introduced into the absorption tube, which for this purpose is inclined and held in one hand, while the bullet is passed into the tube with the other. Care must be taken that the whole of the platinum wire is covered with mercury while the bullet remains in the gas, otherwise there is a risk of air entering the tube between the mercury and the wire (fig. 94).

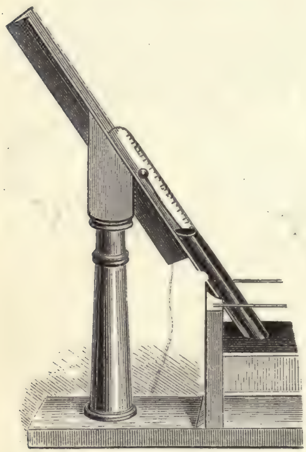


Fig. 94.

After standing for an hour, the bullet is withdrawn from the absorption tube. This must be done with some precaution, so as to prevent any gas being removed from the tube. It is best done by drawing down the bullet by a brisk movement of the wire, the gas being detached from the bullet during the rapid descent of the latter into the mercury. The bullet may then be more slowly removed from the tube. As sodium phosphate and sodium sulphate contain water of crystallization, and a corresponding proportion of this is liberated for every equivalent of sodium chloride formed, care must be taken that the bullets are not too small, else the water set free will soil the sides of the eudiometer, especially if there is a large volume of gas to be absorbed. As a further precaution, drive off some of the water of crystallization before casting the bullet. When the bullet has been removed, the gas must be dried as before with calcium chloride and again measured. If two or more of the gases are present in the mixture to be analyzed, the sodium phosphate ball must be dissolved in water, and the chlorine, bromine, and iodine determined by the ordinary analytical methods. If this has to be done, care must be taken that the sodium phosphate employed is free from chlorine.

Group B. Gases absorbed by Potassium Hydrate, but not by Sodium Phosphate.

Carbonic anhydride, sulphuretted hydrogen, and sulphurous anhydride.

If the gases occur singly, they are determined by means of a bullet

of caustic potash made in the same manner as the sodium phosphate balls. The caustic potash employed should contain sufficient water to render the bullets so soft that they may be marked with the nail when cold. Before use the balls must be slightly moistened with water ; and if large quantities of gas have to be absorbed, the bullet must be removed after some hours, washed with water, and returned to the absorption tube. The absorption may extend over twelve or eighteen hours. In order to ascertain if it is completed, the potash ball is removed, washed, again introduced, and allowed to remain in contact with the gas for about an hour. If no diminution of volume is observed the operation is finished.

The following analysis of a mixture of air and carbonic anhydride will serve to show the mode of recording the observations and the methods of calculation required.

Analysis of a Mixture of Air and Carbonic Anhydride.

I. Gas Saturated with Moisture.

Height of mercury in trough .	=	171·8 mm.
Height of mercury in absorption eudiometer	=	89·0 mm.
Column of mercury in tube, to be subtracted from the height of barometer $=b=$		82·8 mm.
Height of mercury in eudiometer .	=	89·0 mm.
Correction for error of meniscus .	=	0·8 mm.
		89·8 mm.

Volume in table corresponding to 89·8 mm.	$=V=96{\cdot}4$
Temperature at which the reading was made	$=t=12{\cdot}2^\circ$
Height of barometer at time of observation	$=B=765{\cdot}25$ mm.
Tension of aqueous vapour at 12·2°	$=T=$ 10·6 mm.

$$V_1=\frac{V\times(B-b-T)}{1000\times(1+0{\cdot}003665t)}=$$

$$\frac{96{\cdot}4\times(765{\cdot}25-82{\cdot}8-10{\cdot}6)}{1000\times[1+(0{\cdot}003665\times12{\cdot}2)]}=$$

$$\frac{96{\cdot}4\times671{\cdot}85}{1000\times1{\cdot}044713}=61{\cdot}994$$

$$\begin{aligned}
\log.\ 96{\cdot}4 &= 1{\cdot}98408\\
\log.\ 671{\cdot}85 &= 2{\cdot}82727\\
&\overline{\ 4{\cdot}81135\ }\\
\log.\ (1000\times1{\cdot}044713) &= 3{\cdot}01900\\
&\overline{\ 1{\cdot}79235\ }=\log.\ 61{\cdot}994=V_1
\end{aligned}$$

Corrected volume of air and $CO_2=V_1=61{\cdot}994$.

After absorption of carbonic anhydride by bullet of potassium hydrate.

Gas Dry.

Height of mercury in trough .	=	172·0 mm.
Height of mercury in absorption eudiometer	=	62·5 mm.
Column of mercury in eudiometer	$= b =$	109·5 mm.
Height of mercury in eudiometer .	=	62·5 mm.
Correction for error of meniscus .	=	0·8 mm.
		63·3 mm.
Volume in table corresponding to 63·3 mm.	$= V = 69{\cdot}35$	
Temperature	$= t = 10{\cdot}8°$	
Barometer	$= B = 766{\cdot}0$ mm.	

$$V_1 = \frac{V \times (B - b)}{1000 \times (1 + 0{\cdot}003665t)} = \frac{69{\cdot}35 \times (766{\cdot}0 - 109{\cdot}5)}{1000 \times [1 + (0{\cdot}003665 \times 10{\cdot}8)]} = \frac{69{\cdot}35 \times 656{\cdot}5}{1000 \times 1{\cdot}039582} = 43{\cdot}795$$

$$\begin{aligned} \log.\ 69{\cdot}35 &= 1{\cdot}84105 \\ \log.\ 656{\cdot}5 &= 2{\cdot}81723 \\ &\ 4{\cdot}65828 \\ \log.\ (1000 \times 1{\cdot}039582) &= 3{\cdot}01686 \\ &\ 1{\cdot}64142 = \log.\ 43{\cdot}795 = V_1 \end{aligned}$$

$$\begin{aligned} \text{Corrected volume of air} &= 43{\cdot}795 \\ \text{Air} + CO_2 &= 61{\cdot}994 \\ \text{Air} &= 43{\cdot}795 \\ CO_2 &= 18{\cdot}199 \end{aligned}$$

$$61{\cdot}994 : 18{\cdot}199 : : 100 : x = \text{percentage of } CO_2$$

$$x = \frac{18{\cdot}199 \times 100}{61{\cdot}995} = 29{\cdot}355$$

Percentage of CO_2 in mixture of air and gas $= 29{\cdot}355$.

Gas Moist.

Height of mercury in trough .	=	174·0 mm.
Height of mercury in eudiometer .	=	98·0 mm.
Column of mercury in tube . .	$= b =$	76·0 mm.
Height of mercury in eudiometer .	=	98·0 mm.
Correction for error of meniscus . .	=	0·8 mm.
		98·8 mm.

Volume in table, corresponding to 98·8 mm.	$=V=$	105·6
Temperature	$=t=$	12·5°
Barometer	$=B=$	738·0 mm.
Tension of aqueous vapour at 12·5°	$=T=$	10·8 mm.
Corrected volume of air and carbonic anhydride	$=$	65·754

After absorption of CO_2.

II. Gas Dry.

Height of mercury in trough	$=$	173·0 mm.
Height of mercury in absorption eudiometer	$=$	70·3 mm.
Column of mercury in tube	$=b=$	102·7 mm.
Height of mercury in eudiometer	$=$	70·3 mm.
Correction for error of meniscus	$=$	0·8 mm.
		71·1 mm.

Volume in table corresponding to 71·1 mm.	$=V=$	77·4
Temperature	$=t=$	14·1°
Barometer	$=B=$	733·5 mm.

Corrected volume of air $=$ 46·425

Air $+ CO_2 =$ 65·754

Air $=$ 46·425

$CO_2 =$ 19·329

65·754 : 19·329 : : 100 : 29·396.

	I.	II.
Percentage of CO_2 in mixture of air and gas	29·355	29·396

If either sulphurous anhydride or sulphuretted hydrogen occurs together with carbonic anhydride, one or two modes of operation may be followed. Sulphuretted hydrogen and sulphurous anhydride are absorbed by manganic peroxide and by ferric oxide, which may be formed into bullets in the following manner. The oxides are made into a paste with water, and introduced into a bullet mould, the interior of which has been oiled, and containing the coiled end of a piece of platinum wire; the mould is then placed on a sand bath till the ball is dry. The oxides will now be left in a porous condition, which would be inadmissible for the purpose to which they are to be applied; the balls are therefore moistened several times with a syrupy solution of phosphoric acid, care being taken that they do not become too soft, so as to render it difficult to introduce them into the eudiometer. After the sulphuretted hydrogen or sulphurous anhydride has been removed, the gas should be dried by means of calcium chloride. The carbonic anhydride can now be determined by means of the bullet of potassium hydrate.

The second method is to absorb the two gases by means of a ball

of potassium hydrate containing water, but not moistened on the exterior, then to dissolve the bullet in dilute acetic acid which has been previously boiled and allowed to cool without access of air, and to determine the amount of sulphuretted hydrogen or sulphurous anhydride by means of a standard solution of iodine. This process is especially applicable when rather small quantities of sulphuretted hydrogen have to be determined.

Group C. This group contains the gases not absorbed by Potassium Hydrate or Sodium Phosphate, and consists of Oxygen, Nitric Oxide, Carbonic Oxide, Hydrocarbons of the formulæ C_nH_{2n}, $(C_nH_{2n+1})_2$, and C_nH_{2n+2}, except Marsh gas.

OXYGEN was formerly determined by means of a ball of phosphorus, but it is difficult subsequently to free the gas from the phosphorous acid produced, which exerts some tension and so vitiates the results; besides which, the presence of some gases interferes with the absorption of oxygen by phosphorus; and if any potassium hydrate remains on the side of the tube, from the previous absorption of carbonic anhydride, there is a possibility of the formation of phosphoretted hydrogen, which would, of course, vitiate the analysis. A more convenient reagent is a freshly prepared alkaline solution of potassium pyrogallate introduced into the gas in a bullet of papier-maché. The balls of papier-maché are made by macerating filter-paper in water, and forcing as much of it as possible into a bullet mould into which the end of a piece of platinum wire has been introduced. In order to keep the mould from opening while it is being filled, it is well to tie the handles together with a piece of string or wire, and when charged it is placed on a sand bath. After the mass is dry the mould may be opened, when a large absorbent bullet will have been produced. The absorption of oxygen by the alkaline pyrogallate is not very rapid, and it may be necessary to remove the ball once or twice during the operation, and to charge it freshly.

Nitric oxide cannot be readily absorbed in an ordinary absorption tube; it may, however, be converted into nitrous anhydride and nitric peroxide by addition of excess of oxygen, absorbing the oxygen compounds with potassium hydrate, and the excess of oxygen by potassium pyrogallate. The diminution of the volume will give the quantity of nitric oxide. This process is quite successful when the nitric oxide is mixed with olefiant gas and ethylic hydride, but it is possible that other hydrocarbons might be acted on by the nitrous compounds.

Carbonic oxide may be absorbed by two reagents. If carbonic anhydride and oxygen be present they must be absorbed in the usual manner, and afterwards a papier-maché ball saturated with a concentrated solution of cuprous chloride in dilute hydrochloric acid introduced. A ball of caustic potash is subsequently employed to remove the hydrochloric acid given off by the previous

reagent, and to dry the gas. Carbonic oxide may also be absorbed by introducing a ball of potassium hydrate, placing the absorption tube in a beaker of mercury and heating the whole in a water-bath to 100° for 60 hours. The carbonic oxide is thus converted into potassium formate and entirely absorbed.

Olefiant Gas (Ethylene) and other Hydrocarbons of the formula C_nH_{2n} are absorbed by Nordhausen sulphuric acid, to which an additional quantity of sulphuric anhydride has been added. Such an acid may be obtained by heating some Nordhausen acid in a retort connected with a receiver containing a small quantity of the same acid. This liquid is introduced into the gas by means of a dry coke bullet. These bullets are made by filling the mould, into which the usual platinum wire has been placed, with a mixture of equal weights of finely powdered coke and bituminous coal. The mould is then heated as rapidly as possible to a bright red heat, and opened after cooling; a hard porous ball will have been produced, which may be employed for many different reagents. It is sometimes difficult to obtain the proper mixture of coal and coke, but when once prepared, the bullets may be made with the greatest ease and rapidity. The olefiant gas will be absorbed by the sulphuric acid in about an hour, though they may be left in contact for about two hours with advantage. If, on removing the bullet, it still fumes strongly in the air, it may be assumed that the absorption is complete. The gas now contains sulphurous, sulphuric, and perhaps carbonic anhydrides; these may be removed by a manganic peroxide ball, followed by one of potassium hydrate, or the former may be omitted, the caustic potash alone being used. The various members of the C_nH_{2n} group cannot be separated directly, but by the indirect method of analysis their relative quantities in a mixture may be determined.

The hydrocarbons $(C_nH_{2n+1})_2$ and C_nH_{2n+2} may be absorbed by absolute alcohol, some of which is introduced into the absorption tube, and ignited for a short time with the gas. Correction has then to be made for the weight of the column of alcohol on the surface of the mercury, and for the tension of the alcohol vapour. This method only gives approximate results, and can only be employed in the presence of gases very slightly soluble in alcohol.

The time required in the different processes of absorption just described is considerable; perhaps it might be shortened by surrounding the absorption eudiometer with a wider tube, similar to the external tube of a Liebig's condenser, through which a current of water is maintained. By means of a thermometer in the space between the tubes the temperature of the gas would be known, and the readings might be taken two or three minutes after the withdrawal of the reagents. Besides this advantage, the great precaution necessary for maintaining a constant temperature in the room might be dispensed with. A few experiments made some years ago in this direction gave satisfactory results.

INDIRECT DETERMINATIONS.

Gases which are not absorbed by any reagents that are applicable in eudiometers over mercury, must be determined in an indirect manner, by exploding them with other gases, and noting either the change of volume or the quantity of their products of decomposition; or lastly, as is most frequently the case, by a combination of these two methods. Thus, for example, oxygen may be determined by exploding with excess of hydrogen, and observing the contraction; hydrogen may be determined by exploding with excess of oxygen, and measuring the contraction; and marsh gas by exploding with oxygen, measuring the contraction, and also the quantity of carbonic anhydride generated.

The operation is conducted in the following manner:—The long eudiometer furnished with exploding wires is filled with mercury, (after a drop of water has been placed at the top of the tube by means of an iron wire, as before described), and some of the gas to be analyzed is introduced from the absorption eudiometer. This gas is then measured with the usual precautions, and an excess of oxygen or hydrogen (as the case may be) introduced. These gases may be passed into the eudiometer directly from the apparatus in which they are prepared; or they may be previously collected in lipped tubes of the form of absorption tubes, so as to be always ready for use.

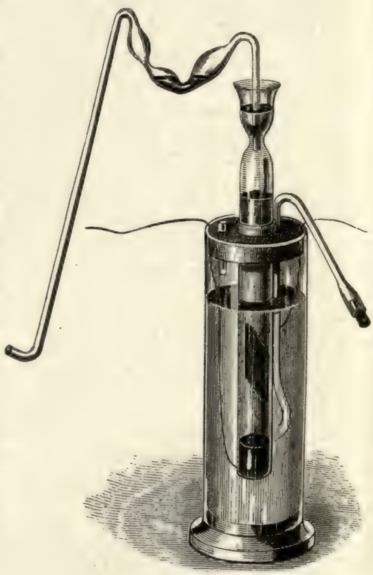


Fig. 95.

For the preparation of the oxygen a bulb is used, which is blown at the closed end of a piece of combustion tube. The bulb is about half filled with dry powdered potassium chlorate, the neck drawn out, and bent to form a delivery tube. The chlorate is fused, and the gas allowed to escape for some time to ensure the expulsion of the atmospheric air; the end of the delivery tube is then brought under the orifice of the eudiometer, and the necessary quantity of gas admitted. When it is desired to prepare the oxygen beforehand, it may be collected directly from the bulb; or, another method to obtain the gas free from air may be adopted by those who are provided with the necessary appliances. This is, to connect a bulb containing potassium chlorate with a Sprengel's mercurial air-pump, and,

after heating the chlorate to fusion, to produce a vacuum in the apparatus. The chlorate may be again heated until oxygen begins to pass through the mercury at the end of the Sprengel, the heat then withdrawn, and a vacuum again obtained. The chlorate is once more heated, and the oxygen collected at the bottom of the Sprengel. Of course the usual precautions for obtaining an air-tight joint between the bulk and the Sprengel must be taken, such as surrounding the caoutchouc connector with a tube filled with mercury.

The hydrogen for these experiments must be prepared by electrolysis, since that from other sources is liable to contamination with impurities which would vitiate the analysis. The apparatus employed by Bunsen for this purpose (fig. 95) consists of a glass tube, closed at the lower end, and with a funnel at the other, into which a delivery tube is ground, the funnel acting as a water-joint. A platinum wire is sealed into the lower part of the tube; and near the upper end another wire, with a platinum plate attached, is fused into the glass. Some amalgam of zinc is placed in the tube so as to cover the lower platinum wire, and the apparatus filled nearly to the neck with water acidulated with sulphuric acid. On connecting the platinum wires with a battery of two or three cells, the upper wire being made the negative electrode, pure hydrogen is evolved from the platinum plate, and, after the expulsion of the air, may be at once passed into the eudiometer, or, if preferred, collected in tubes for future use. Unfortunately, in this form of apparatus the zinc amalgam soon becomes covered with a saturated solution of zinc sulphate, which puts a stop to the electrolysis. In order to remove this layer, Bunsen has a tube fused into the apparatus at the surface of the amalgam; this is bent upwards parallel to the larger tube, and curved downwards just below the level of the funnel. The end of the tube is closed with a caoutchouc stopper. On removing the stopper, and pouring fresh acid into the funnel, the saturated liquid is expelled.

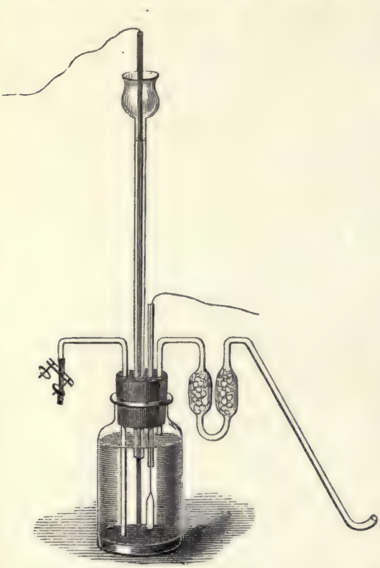


Fig. 96.

Another form of apparatus for preparing electrolytic hydrogen may readily be constructed. A six-ounce wide-mouth bottle is

fitted with a good cork, or better, with a caoutchouc stopper. In the stopper four tubes are fitted (fig. 96). The first is a delivery tube, provided with a U-tube, containing broken glass and sulphuric acid, to conduct the hydrogen to the mercurial trough. The second tube about 5 centimetres long, and filled with mercury, has fused into its lower end a piece of platinum wire carrying a strip of foil, or the wire may be simply flattened. The third tube passes nearly to the bottom of the bottle, the portion above the cork is bent twice at right-angles, and cut off, so that the open end is a little above the level of the shoulder of the bottle ; a piece of caoutchouc tube, closed by a compression cock, is fitted to the end of the tube. The fourth tube is a piece of combustion tube about 30 centimetres in length, which may with advantage be formed into a funnel at the top. This tube reaches about one-third down the bottle, and inside it is placed a narrower glass tube, attached at its lower end by a piece of caoutchouc connector to a rod of amalgamated zinc. The tube is filled with mercury to enable the operator readily to connect the zinc with the battery ; some zinc amalgam is placed at the bottom of the bottle ; and dilute sulphuric acid is poured in through the wide tube until the bottle is nearly filled with liquid. To use the apparatus, the delivery tube is dipped into mercury, the wire from the positive pole of the battery put into the mercury in the tube to which the zinc is attached, and the negative pole connected by means of mercury with the platinum plate. The current, instead of passing between the amalgam at the bottom of the vessel and the platinum plate, as in Bunsen's apparatus, travels from the rod of amalgamated zinc to the platinum, consequently the current continues to flow until nearly the whole of the liquid in the bottle has become saturated with zinc sulphate. As soon as the hydrogen is evolved, of course a column of acid is raised in the funnel until the pressure is sufficient to force the gas through the mercury in which the delivery tube is placed. Care must be taken that the quantity of acid in the bottle is sufficient to prevent escape of gas through the funnel tube, and also that the delivery tube does not pass too deeply into the mercury so as to cause the overflow of the acid. When the acid is exhausted, the compression cock on the bent tube is opened and fresh acid poured into the funnel ; the dense zinc sulphate solution is thus replaced by the lighter liquid, and the apparatus is again ready for use.

A very convenient apparatus for transferring oxygen and hydrogen into eudiometers is a gas pipette, figured and described (fig. 68, p. 459).

It is necessary in all cases to add an excess of the oxygen or hydrogen before exploding, and it is well to be able to measure approximately the amount added without going through the whole of the calculations. This may be conveniently done by making a rough calibration of the eudiometer in the following manner :—The tube is filled with mercury, a volume of air introduced into it

from a small tube, and the amount of the depression of the mercury noted ; a second volume is now passed up, a further depression will be produced, but less in extent than the previous one, in consequence of the shorter column of mercury in the tube. This is repeated until the eudiometer is filled, and by means of a table constructed from these observations, but without taking any notice of the variations of thermometer or barometer, the operator can introduce the requisite quantity of gas. It may be convenient to make this calibration when the eudiometer is inclined in the support, and also when placed perpendicularly, so that the gas may be introduced when the tube is in either position. A table like the following is thus obtained :—

DIVISIONS.

Measures.	Tube Inclined.	Tube Perpendicular.
1	27	45
2	45	69
3	61	87
4	75	102
5	88	116
6	100	128
7	109	138
&c.	&c.	&c.

In explosions of hydrocarbons with oxygen, it is necessary to have a considerable excess of the latter gas in order to moderate the violence of the explosion. The same object may be attained by diluting the gas with atmospheric air, but it is found that sufficient oxygen serves equally well. If the gas contains nitrogen, it is necessary subsequently to explode the residual gas by hydrogen ; and if oxygen only has been used for diluting the gas, a very large quantity of hydrogen must be added, which may augment the volume in the eudiometer to an inconvenient extent. When atmospheric air has been employed, this inconvenience is avoided. After the introduction of the oxygen, the eudiometer is restored to its vertical position, allowed to stand for an hour, and the volume read off.

The determination of the quantity of oxygen which must be added to combustible gases so as to prevent the explosion from being too violent, and at the same time to ensure complete combustion, has been made the subject of experiment. When the gases before explosion are under a pressure equal to about half that of the atmosphere, the following proportions of the gases must be employed :—

	Volume of Combustible Gas.	Volume of Oxygen.
Hydrogen	1	1·5
Carbonic oxide	1	1·5
Marsh gas	1	5

	Volume of Combustible Gas.	Volume of Oxygen.
Gases containing two atoms of carbon in the molecule, as Ethane C_2H_6 . . .	1	10
Gases containing three atoms of carbon in the molecule, as Propyl hydride, C_3H_8 . .	1	18
Gases containing four atoms of carbon in the molecule, as Butane, C_4H_{10} . .	1	25

In cases of mixtures of two or more combustible gases proportionate quantities of oxygen must be introduced.

Fig. 97.

At the time of the explosion, it is necessary that the eudiometer should be carefully closed to prevent the loss of gas by the sudden expansion. For this purpose a thick plate of caoutchouc, three or four centimetres wide, is cemented on a piece of cork by means of marine glue, or some similar substance, and the lower surface of the cork cut so as to lie firmly at the bottom of the mercurial trough (fig. 97). It is, however, preferable to have the caoutchouc firmly fixed in the trough. As the mercury does not adhere to the caoutchouc, there is some risk of air entering the eudiometer after the explosion; this is obviated by rubbing the plate with some solution of corrosive sublimate before introducing it into the mercury, which causes the metal to wet the caoutchouc and removes all air from its surface. When the caoutchouc is not fixed in the trough, the treatment with the corrosive sublimate has to be repeated before every experiment, and this soils the surface of the mercury to an inconvenient extent. The cushion is next depressed to the bottom of the trough, and the eudiometer placed on it and firmly held down (fig. 98). If this is done with the hands, the tube must be held by that portion containing the mercury, for it is found that when eudiometers burst (which, however, only happens when some precaution has been neglected) they invariably give way just at the level of the mercury within the tube, and serious accidents might occur if the hands were at this point. The cause of the fracture at this point is the following:—Though the gas is at a pressure below that of the atmosphere before the explosion,

Fig. 98.

yet at the instant of the passage of the spark, the expansion of the gas at the top of the tube condenses the layer just below it; this on exploding increases the density of the gas further down the tube, and, by the time the ignition is communicated to the lowest quantity of gas, it may be at a pressure far above that of the atmosphere. It may be thought that the explosion is so instantaneous that this explanation is merely theoretical; but on exploding a long column of gas, the time required for the complete ignition is quite perceptible, and sometimes the flash may be observed to be more brilliant at the surface of the mercury. Some experimenters prefer to fix the eudiometer by means of an arm from a vertical stand, the arm being hollowed out on the under side, and the cavity lined with cork.

If a large quantity of incombustible gas is present, the inflammability of the mixture may be so much reduced that either the explosion does not take place at all, or, what may be worse, only a partial combustion ensues. To obviate this, some explosive mixture of oxygen and hydrogen, obtained by the electrolysis of water, must be introduced. The apparatus used by Bunsen for this purpose is shown in fig. 99. The tube in which the electrolysis takes place is surrounded by a cylinder containing alcohol, in order to prevent the heating of the liquid. A convenient apparatus for the preparation of this gas is made by blowing a bulb of about four centimetres in diameter on the end of a piece of narrow glass tube, sealing two pieces of flattened platinum wire into opposite sides of the globe, and bending the tube so as to form a delivery tube. Dilute sulphuric acid, containing about one volume of acid to twenty of water, is introduced into the globe, either before bending the tube, by means of a funnel with a fine long stem, or, after the bending, by warming the apparatus, and plunging the tube into the acid. Care must be taken that the acid is dilute, and that the battery is not too strong, in order to avoid the formation of ozone, which

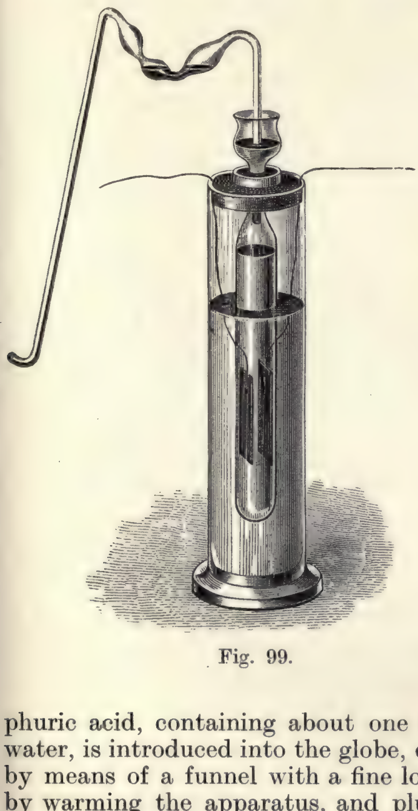


Fig. 99.

would attack the mercury, causing the sides of the eudiometer to be soiled, at the same time producing a gas too rich in hydrogen.

The spark necessary to effect the explosion may be obtained from several sources. An ordinary electrical machine or electrophorus may be used, but these are liable to get out of order by damp. Bunsen uses a porcelain tube, which is rubbed with a silk rubber, coated with electrical amalgam; by means of this a small Leyden jar is charged. A still more convenient apparatus is an induction coil large enough to produce a spark of half an inch in length.

After the explosion, the eudiometer is slightly raised from the caoutchouc plate to allow the entrance of mercury. When no more mercury rushes in, the tube is removed from the caoutchouc plate, placed in a perpendicular position, and allowed to remain for at least an hour before reading. After measuring the contraction, it is generally necessary to absorb the carbonic anhydride formed by the combustion by means of a potash ball, in the way previously described. In some rare instances the amount of water produced in the explosion with oxygen must be measured. If this has to be done, the eudiometer, the mercury, the original gas, and the oxygen must all be carefully dried. After the explosion, the eudiometer is transferred to a circular glass vessel containing mercury, and attached to an iron-wire support, by which the entire arrangement can be suspended in a glass tube adapted to the top of an iron boiler, from which a rapid current of steam may be passed through the glass tube, so as to heat the eudiometer and mercury to an uniform temperature of 100°. From the measurements obtained at this temperature the amount of water produced may be calculated. If three combustible gases are present, the only data required for calculation are, the original volume of the gas, the contraction on explosion, and the amount of carbonic anhydride generated. When the original gas contains nitrogen, the residue after explosion with excess of oxygen consists of a mixture of oxygen and nitrogen. To this an excess of hydrogen is added, and the mixture exploded; the contraction thus produced divided by 3 gives the amount of oxygen in the residual gas, and the nitrogen is found by difference.

It is obvious that, by subtracting the quantity of residual oxygen, thus determined by explosion with hydrogen, from the amount added, in the first instance, to the combustible gas, the volume of oxygen consumed in the explosion may be obtained. Some chemists prefer to employ this number instead of the contraction as one of the data for the calculation.

We must now glance at the mode of calculation to be employed for obtaining the percentage composition of a gas from the numbers arrived at by the experimental observations.

The following table shows the relations existing between the volume of the more important combustible gases and the products of the explosion :—

Name of Gas.	Volume of Combustible Gas.	Volume of Oxygen Consumed.	Contraction after Explosion.	Volume of Carbonic Anhydride produced.
Hydrogen, H_2	1	0·5	1·5	0
Carbonic Oxide, CO	1	0·5	0·5	1
Methane, CH_4	1	2	2	1
Acetylene, C_2H_2	1	2·5	1·5	2
Ethylene, C_2H_4	1	3	2	2
Ethane, CH_3, CH_3	1	3·5	2·5	2
Ethyl Hydride, C_2H_5H . .	1	3·5	2·5	2
Propylene, C_3H_6	1	4·5	2·5	3
Propyl Hydride, C_3H_7H . .	1	5	3	3
Butylene, C_4H_8	1	6	3	4
Butane, C_2H_5, C_2H_5	1	6·5	3·5	4
Butyl Hydride, C_4H_9H . .	1	6·5	3·5	4

As an example, we may take a mixture of hydrogen, carbonic oxide, and methane, which gases may be designated by x, y, and z respectively. The original volume of gas may be represented by A, the contraction by C, and the amount of carbonic anhydride by D.

A will of course be made up of the three components, or

$$A = x + y + z.$$

C will be composed as follows :—When a mixture of 2 volumes of hydrogen and 1 volume of oxygen is exploded, the gas entirely disappears. One volume of hydrogen combining with half a volume of oxygen, the contraction will be $1\frac{1}{2}$ times the quantity of hydrogen present, or $1\frac{1}{2}x$. In the case of carbonic oxide, 1 volume of this gas uniting with half its volume of oxygen produces 1 volume of carbonic anhydride, so the contraction due to the carbonic oxide will be half its volume, or $\frac{1}{2}y$. Lastly, 1 volume of marsh gas combining with 2 volumes of oxygen generates 1 volume of carbonic anhydride, so the contraction in this case will be twice its volume, or $2x$. Thus we have—

$$C = 1\tfrac{1}{2}x + \tfrac{1}{2}y + 2z.$$

Since carbonic oxide on combustion forms its own volume of carbonic anhydride, the amount produced by the quantity present in the mixture will be y. Marsh gas also generates its own volume of carbonic anhydride, so the quantity corresponding to the marsh gas in the mixture will be z. Therefore

$$D = y + z.$$

It now remains to calculate the values of x, y, and z from the experimental numbers A, C, and D, which is done by the help of the following equations :—

$$A = x + y + z. \qquad C = 1\tfrac{1}{2}x + \tfrac{1}{2}y + 2z. \qquad D = y + z.$$

To find x—

$$\begin{array}{rl} x+y+z &= A, \\ y+z &= D, \\ \hline x \qquad &= A-D. \end{array}$$

For y we have—

$$\begin{array}{rl} 4y+4z &= 4D, \\ 3x+\ \ y+4z &= 2C, \\ \hline -3x+3y \qquad &= 4D-2C, \\ 3x \qquad\qquad &= 3A-3D, \\ \hline 3y \qquad &= 3A-2C+D, \text{ or} \end{array}$$

$$y=\frac{3A-2C+D}{3}.$$

The value of z is thus found—

$$D=y+z \therefore$$
$$z=D-y=$$
$$D-\frac{3A-2C+D}{3}, \text{ or}$$
$$z=\frac{2C-3A+2D}{3}.$$

By replacing the letters A, C, and D by the numbers obtained by experiment, the quantities of the three constituents in the volume A may easily be calculated by the three formulæ—

$$x=A-D \qquad =\text{hydrogen},$$
$$y=\frac{3A-2C+D}{3}=\text{carbonic oxide},$$
$$z=\frac{2C-3A+2D}{3}=\text{methane},$$

The percentage composition is, of course, obtained by the simple proportions—

A : x : : 100 : per-cent. of hydrogen,
A : y : : 100 : per-cent. of carbonic oxide,
A : z : : 100 : per-cent. of methane.

If the gas had contained nitrogen, it would have been determined by exploding the residual gas, after the removal of the carbonic anhydride, with excess of hydrogen. The contraction observed, divided by 3, would give the volume of oxygen in the residue, and this deducted from the residue, would give the amount of nitrogen. If A again represents the original gas, and n the amount of nitrogen it contains, the expression $A-n$ would have to be substituted for A in the above equations.

It may be as well to develop the formulæ for obtaining the same results by observing the volume of oxygen consumed instead of the contraction. If B represents the quantity of oxygen, we shall have

$$B=\tfrac{1}{2}x+\tfrac{1}{2}y+2z,$$

the values of A and D remaining as before, $x=A-D$.

z is thus found—

$$\begin{aligned} x+y+4z &= 2B, \\ x+y+\ z &= A, \\ \hline 3z &= 2B-A, \quad \text{or} \\ z &= \frac{2B-A}{3}. \end{aligned}$$

For y—

$$\begin{aligned} D &= y+z \\ y &= D-z = \\ & D-\frac{2B-A}{3}, \quad \text{or} \\ y &= \frac{3D-2B+A}{3} \end{aligned}$$

Thus we have—

$$\begin{aligned} x &= A-D \\ y &= \frac{3D-2B+A}{3} \\ z &= \frac{2B-A}{3} \end{aligned}$$

Having thus shown the mode of calculation of the formulæ, it will be well to give some examples of the formulæ employed in some of the cases which most frequently present themselves in gas analysis. In all cases—

A = original mixture,
C = contraction,
D = carbonic anhydride produced.

1. Hydrogen and Nitrogen.

$$H=x;\ N=y.$$

Excess of oxygen is added, and the contraction on explosion observed :—

$$x=\frac{2C}{3},$$
$$y=\frac{3A-2C}{3}, \text{ or } A-x.$$

2. Carbonic Oxide and Nitrogen.

$$CO=x;\ N=y.$$

The gas is exploded with excess of oxygen, and the amount of carbonic anhydride produced is determined;

$$x=D,$$
$$y=A-D.$$

3. Hydrogen, Carbonic Oxide, and Nitrogen.

$$H=x;\ CO=y;\ N=z.$$

In this case the contraction and the quantity of carbonic anhydride are measured :—

$$x=\frac{2C-D}{3},$$
$$y=D,$$
$$z=\frac{3A-2C-2D}{3}.$$

4. Hydrogen, Methane, and Nitrogen.

$$H=x;\ CH_4=y;\ N=z.$$

$$x=\frac{2C-4D}{3},$$
$$y=D,$$
$$z=\frac{3A-2C+D}{3}.$$

5. Carbonic Oxide, Methane, and Nitrogen.

$$CO=x;\ CH_4=y;\ N=z.$$

$$x=\frac{4D-2C}{3},$$
$$y=\frac{2C-D}{3},$$
$$z=A-D.$$

6. Hydrogen, Ethane (or Ethyl Hydride), and Nitrogen.

$$H=x;\ C_2H_6=y;\ N=z.$$

$$x=\frac{4C-5D}{6},$$
$$y=\frac{D}{2},$$
$$z=\frac{3A-2C+D}{3}.$$

7. Carbonic Oxide, Ethane (or Ethyl Hydride), and Nitrogen.

$$CO=x;\ C_2H_6=y;\ N=z.$$

$$x=\frac{5D-4C}{3},$$
$$y=\frac{2C-D}{3},$$
$$z=\frac{3A-4D+2C}{3}.$$

8. Hydrogen, Carbonic Oxide, and Methane.

$$H=x;\ CO=y;\ CH_4=z.$$

$$x=A-D,$$
$$y=\frac{3A-2C+D}{3},$$
$$z=\frac{2C-3A+2D}{3}.$$

9. Hydrogen, Carbonic Oxide, and Ethyl Hydride (or Ethane).

$$H=x;\ CO=y;\ C_2H_6=z.$$

$$x=\frac{3A+2C-4D}{6},$$
$$y=\frac{3A-2C+D}{3},$$
$$z=\frac{2C-3A+2D}{6}.$$

10. Carbonic Oxide, Methane, and Ethyl Hydride (or Ethane).

$$CO=x;\ CH_4=y;\ C_2H_6=z.$$

$$x=\frac{3A-2C+D}{3},$$
$$y=\frac{3A+2C-4D}{3},$$
$$z=D-A.$$

11. Hydrogen, Methane, and Acetylene.

$$H=x;\ CH_4=y;\ C_2H_2=z.$$

$$x=\frac{5A-2C-D}{2},$$
$$y=2C-3A,$$
$$z=\frac{D-2C+3A}{2}.$$

12. Hydrogen, Methane, and Ethyl Hydride (or Ethane).

$$H=x;\ CH_4=y;\ C_2H_6=z.$$

This mixture cannot be analyzed by indirect determination, since a mixture of two volumes of hydrogen with two volumes of ethyl

hydride (or ethane) has the same composition as four volumes of methane—

$$C_2H_6+H_2=2CH_4 ;$$

and, consequently, would give rise to the same products on combustion with oxygen as pure methane—

$$C_2H_6+H_2+4O_2=2CO_2+4OH_2 ;$$
$$2CH_4+4O_2=2CO_2+4OH_2.$$

In this case it is necessary to determine directly the ethyl hydride (or ethane) in a separate portion of the gas by absorption with alcohol, another quantity of the mixture being exploded with oxygen, and the amount of carbonic anhydride produced measured. If the quantity absorbed by alcohol$=$E, then

$$x=A-D+E,$$
$$y=D-2E,$$
$$z=E.$$

13. Hydrogen, Carbonic Oxide, Propyl Hydride.

$$H=x ;\ CO=y ;\ C_3H_8=z.$$

$$x=\frac{3A+4C-5D}{9},$$
$$y=\frac{3A-2C+D}{3},$$
$$z=\frac{2C-3A+2D}{9}.$$

14. Carbonic Oxide, Methane, and Propyl Hydride.

$$CO=x ;\ CH_4=y ;\ C_3H_8=z.$$

$$x=\frac{3A-2C+D}{3},$$
$$y=\frac{3A+4C-5D}{6},$$
$$z=\frac{D-A}{2}.$$

15. Carbonic Oxide, Ethyl Hydride (or Ethane), and Propyl Hydride.

$$CO=x ;\ C_2H_6=y ;\ C_3H_8=z.$$

$$x=\frac{3A-2C+D}{3},$$
$$y=\frac{3A+4C-5D}{3},$$
$$z=\frac{4D-3A-2C}{3}.$$

16. Methane, Ethyl Hydride (or Ethane), and Propyl Hydride.

$$CH_4=x;\ C_2H_6=y;\ C_3H_8=z.$$

As a mixture of two volumes of methane and two of propyl hydride has the same composition as four of ethyl hydride (or ethane)—

$$CH_4+C_3H_8=2C_2H_6,$$

the volume absorbed by alcohol, which consists of ethyl hydride (or ethane) and propyl hydride, must be determined, and another portion of the gas exploded, and the contraction measured. If E represents the volume absorbed—

$$x=A-E,$$
$$y=4A-2C+2E,$$
$$z=2C+4A-E.$$

17. Hydrogen, Carbonic Oxide, and Butane (or Butyl Hydride).

$$H=x;\ CO=y;\ C_4H_{10}=z.$$

$$x=\frac{A+2C-2D}{4},$$
$$y=\frac{3A-2C+D}{3},$$
$$z=\frac{2C+2D-3A}{12}.$$

18. Nitrogen, Hydrogen, Carbonic Oxide, Ethyl Hydride (or Ethane), and Butyl Hydride (or Butane).

$$N=n;\ H=w;\ CO=x;\ C_2H_6=y;\ C_4H_{10}=z.$$

In one portion of the gas the ethyl hydride (or ethane) and the butyl hydride (or butane) are absorbed by alcohol; the amount absorbed = E.

A second portion of the original gas is mixed with oxygen and exploded, the amount of contraction and of carbonic anhydride being measured.

The residue now contains the nitrogen and the excess of oxygen; to this an excess of hydrogen is added, the mixture exploded, and the contraction measured. From this the quantity of nitrogen is thus obtained. Let—

G = excess of oxygen and nitrogen,
v = excess of oxygen,
n = nitrogen,
C_1 = contraction on explosion with hydrogen.

Then—

$$G = v + n,$$
$$C_1 = 3v,$$
$$3v = C_1$$
$$v = \frac{C_1}{3},$$
$$n = G - v = G - \frac{C_1}{3} = \frac{3G - C_1}{3}.$$

From these data the composition of the mixture can be determined—

$$w = \frac{2C - D - 3E}{3},$$
$$x = \frac{3A - 2C + D - 3n}{3},$$
$$y = \frac{3A - 2C - 2D + 12E - 3n}{6},$$
$$z = \frac{2C - 3A + 2D - 6E + 3n}{6}.$$

MODIFICATIONS AND IMPROVEMENTS OF THE FOREGOING PROCESSES.

In the method of gas analysis that we have been considering, the calculations of results are somewhat lengthy, as will be seen by a reference to the example given of the analysis of a mixture of air and carbonic anhydride (page 521). Besides this, the operations must be conducted in a room of uniform temperature, and considerable time allowed to elapse between the manipulation and the readings in order to allow the eudiometers to acquire the temperature of the surrounding air; and, lastly, the absorption of gases by solid reagents is slow. These disadvantages are to a great extent counterbalanced by the simplicity of the apparatus and of the manipulation.

From time to time various chemists have proposed methods by which the operations are much hastened and facilitated, and the calculations shortened. It will be necessary to mention a few of these processes, which, however, require special forms of apparatus.

Williamson and Russell* have described an apparatus, by means of which the gases in the eudiometers are measured under a constant pressure, the correction for temperature being eliminated by varying the column of mercury in the tube so as to compensate for the alteration of volume observed in a tube containing a standard volume of moist air. In this case solid reagents were employed in the eudiometers.

* *Proceedings of the Royal Society*, **9**, 218.

In 1864 they published* a further development of this method, in which the absorptions were conducted in a separate laboratory vessel, by which means the reagents could be employed in a pasty condition and extended over a large surface. And in 1868 Russell† improved the apparatus, so that liquid reagents could be used in the eudiometers, and the analysis rapidly executed.

The gutta-percha mercury trough employed is provided with a deep well, into which the eudiometer can be depressed to any required extent, and on the surface of the mercury a wide glass cylinder, open at both ends and filled with water, is placed. The eudiometer containing the gas to be examined is suspended within the cylinder of water by means of a steel rod passing through a socket attached to a stout standard firmly fixed to the table. In a similar manner, a tube containing moist air is placed by the side of the eudiometer. The clamp supporting this latter tube is provided with two horizontal plates of steel, at which the column of the mercury is read off. When a volume of gas has to be measured, the pressure tube containing the moist air is raised or lowered, by means of an ingeniously contrived fine adjustment, until the mercury stands very nearly at the level of one of the horizontal steel plates. The eudiometer is next raised or lowered until the column of mercury within it is at the same level. The final adjustment to bring the top of the meniscus exactly to the lower edge of the steel bar is effected by sliding a closed wide glass tube into the mercury trough. Thus we have two volumes of gas under the same pressure and temperature, and both saturated with moisture. If the temperature of the water in the cylinder increased, there would be a depression of the columns in both tubes ; but by lowering the tubes, and thus increasing the pressure until the volume of air in the pressure tube was the same as before, it would be found that the gas in the eudiometer was restored to the original volume. Again, if the barometric pressure increased, the volumes of the gases would be diminished ; but, by raising the tubes to the necessary extent, the previous volumes would be obtained. Therefore, in an analysis, it is only necessary to measure the gas at a pressure equal to that which is required to maintain the volume of moist air in the pressure tube constant. The reagents are introduced into the eudiometer in the liquid state by means of a small syringe made of a piece of glass tube about one-eighth of an inch in diameter. For this purpose the eudiometer is raised until its open end is just below the surface of the mercury, and the syringe, which is curved upwards at the point, is depressed in the trough, passed below the edge of the water cylinder, and the extremity of the syringe introduced into the eudiometer. When a sufficient quantity of the liquid has been injected, the eudiometer is lowered and again raised, so as to moisten the sides of the tube with the liquid, and thus hasten the absorption. Ten minutes was found to

* *J. C. S.* **17**, 238. † *J. C. S.* **21**, 128.

be a sufficient time for the absorption of carbonic anhydride when mixed with air.

To remove the liquid reagent, a ball of moistened cotton wool is employed. The ball is made in the following manner :—A piece of steel wire is bent into a loop at one end, and some cotton wool tightly wrapped around it. It is then dipped in water and squeezed with the hand under the liquid until the air is removed. The end of the steel wire is next passed through a piece of glass tube, curved near one end and the cotton ball drawn against the curved extremity of the tube. The ball, saturated with water, is now depressed in the mercury trough, and, after as much of the water as possible has been squeezed out of it, it is passed below the eudiometer, and, by pushing the wire, the ball is brought to the surface of the mercury in the eudiometer and rapidly absorbs all the liquid reagent, leaving the meniscus clean. The ball is removed with a slight jerk, and gas is thus prevented from adhering to it. It is found that this mode of removing the liquid can be used without fear of altering the volume of the gas in the eudiometer.

Carbonic anhydride may be absorbed by a solution of potassium hydrate, and oxygen by means of potassium hydrate and pyrogallic acid. The determination of ethylene is best effected by means of fuming sulphuric acid on a coke ball, water and dilute potassium hydrate being subsequently introduced and removed by the ball of cotton wool.

Doubtless this mode of using the liquid reagents might be employed with advantage in the ordinary process of analysis to diminish the time necessary for the absorption of the gases. By this process of Russell's the calculations are much shortened and facilitated, the volumes read off being comparable among themselves; this will be seen by an example, taken from the original memoir, of the determination of oxygen in air—

		Volume in Table corresponding to reading.
Volume of air taken . . .	130·3	132·15
Volume after absorption of oxygen by potassium hydrate and pyrogallic acid	103·5	104·46

132·15
104·46

27·69 volumes of oxygen in 132·15 of air

132·15 : 27·69 : : 100 : 20·953 percentage of oxygen in air.

Russell* has also employed his apparatus for the analysis of carbonates. For this purpose he adapted a graduated tube, open at both ends, to a glass flask by means of a thick piece of rubber tube. Into the flask a weighed quantity of a carbonate was placed, together with a vessel containing dilute acid. The position of the mercury in the graduated tube was first read off, after which the flask was shaken so as to bring the acid and carbonate in contact,

* *J. C. S.* [N.S.] 6, 310.

and the increase in volume was due to the carbonic anhydride evolved. The results thus obtained are extremely concordant.

In eight experiments with sodium carbonate the percentage of carbonic anhydride found varied from 41·48 to 41·61, theory requiring 41·51.

Thirteen experiments with calc-spar gave from 43·52 to 43·86, the theoretical percentage being 44·0; and in nine other analyses from 43·58 to 43·90 were obtained.

Two experiments were made with manganic peroxide, oxalic acid, and sulphuric acid, and gave 58·16 and 58·10 per cent. of carbonic anhydride.

Some determinations of the purity of magnesium were also performed by dissolving the metal in hydrochloric acid and measuring the resulting hydrogen. Four operations gave numbers varying between 8·26 and 8·28. The metal should yield 8·33.

Russell* has also employed this process for the determination of the combining proportions of nickel and cobalt.

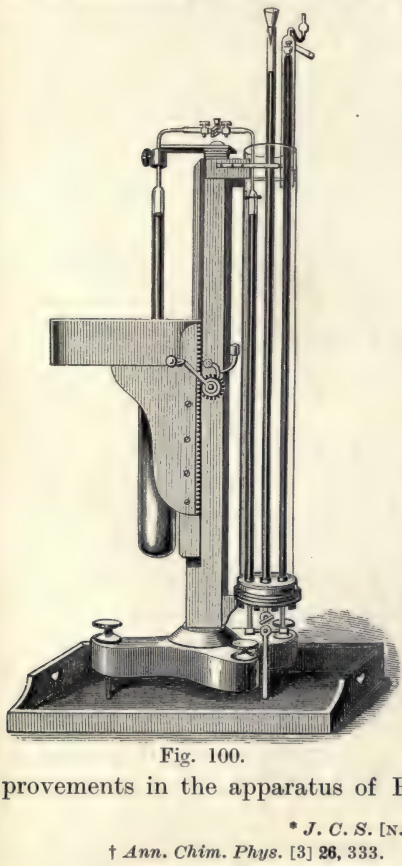


Fig. 100.

Regnault and Reiset† described an apparatus by which absorptions could be rapidly conducted by means of liquid reagents brought in contact with the gases in a laboratory tube. The measurements are made in a graduated tube, which can be placed in communication with the laboratory tube by means of fine capillary tubes provided with stop-cocks, the lower end of the measuring tube being connected by an iron socket and stop-cock with another graduated tube in which the pressure to which the gas is subjected is measured. The measuring and pressure tubes are surrounded by a cylinder of water. An apparatus similar in principle to this has recently been constructed by Frankland, and is fully described in the section on Water Analysis (fig. 64, p. 454).

Frankland and Ward‡ made several important improvements in the apparatus of Regnault and Reiset. They

* *J. C. S.* [N.S.] **7**, 294.

† *Ann. Chim. Phys.* [3] **26**, 333.

‡ *J. C. S.* **6**, 197.

introduced a third tube (fig. 100), closed at the top with a stopper, which is made to act as a barometer, to indicate the tension of the gas in the measuring tube, thus rendering the operation entirely independent of variations of atmospheric pressure. The correction for aqueous vapour is also eliminated by introducing a drop of water into the barometer as well as into the measuring tube, the pressures produced by the aqueous vapour in the two tubes thus counterbalancing one another, so that the difference of level of the mercury gives at once the tension of the dry gas. The measuring tube is divided into ten equal divisions (which, for some purposes, require to be calibrated), and in one analysis it is convenient to make all the measurements at the same division, or to calculate the tension which would be exerted by the gas if measured at the tenth division. Frankland and Ward also adapted an iron tube more than 760 mm. long at the bottom of the apparatus, which enables the operator to expand the gas to any required extent, and thus diminish the violence of the explosions which are performed in the measuring tube. During the operation a constant stream of water is kept flowing through the cylinder, which maintains an uniform temperature.

By the use of this form of apparatus the calculations of analyses are much simplified. An example of an analysis of atmospheric air will indicate the method of using the instrument.

Volume of Air used. Determined at 5th Division on the Measuring Tube.

	mm.
Observed height of mercury in barometer .	673·0
Height of 5th Division	383·0
Tension of gas . . .	290·0
	0·5
Corrected tension of gas at 10th division . .	145·00

Volume after Admission of Hydrogen. Determined at 6th Division.

	mm.
Observed height of mercury in barometer .	772·3
Height of 6th Division	304·0
Tension of gas . . .	468·3
	0·6
Corrected tension at 10th division . . .	280·98

Volume after explosion. Determined at 5th Division.

	mm.
Observed height of mercury in barometer .	763·3
Height of 5th Division	383·0
Tension of gas . . .	380·3
	0·5
Corrected tension at 10th division . . .	190·15

Tension of air with hydrogen	280·98
Tension of gas after explosion	190·15
Contraction on explosion	90·83

of which one-third is oxygen.

$$\frac{90{\cdot}83}{3}=30{\cdot}276=\text{volumes of oxygen in }145{\cdot}0\text{ volumes of air}$$

$$145{\cdot}0 \ : \ 30{\cdot}276 \ :: \ 100 \ : \ x$$

$$x=\frac{30{\cdot}276\times 100}{145{\cdot}0}=20{\cdot}88=\text{percentage of oxygen in air.}$$

If all the measurements had been made at the same division, no correction to the tenth division would have been necessary, as the numbers would have been comparable among themselves.

Another modification of Frankland and Ward's, or Regnault's apparatus has been designed by McLeod,* in which the original pressure tube of Regnault's apparatus, or the filling tube of Frankland and Ward, is dispensed with, the mercury being admitted to the apparatus through the stop-cocks at the bottom.

The measuring tube A (fig. 101) is 900 mm. in length, and about 20 mm. in internal diameter. It is marked with ten divisions, the first at 25 mm. from the top, the second at 50, the third at 100, and the remaining ones at intervals of 100 mm. In the upper part of the tube, platinum wires are sealed, and it is terminated by a capillary tube and a fine glass stop-cock, *a*, the capillary tube being bent at right-angles at 50 mm. above the junction. At the bottom of the tube, a wide glass stop-cock *b* is sealed, which communicates, by means of a caoutchouc joint surrounded with tape and well wired to the tubes, with a branch from the barometer tube B. This latter tube is 5 mm. in width, and about 1200 mm. long, and is graduated in millimetres from bottom to top. At the upper extremity a glass stop-cock *d* is joined, the lower end being curved and connected by caoutchouc with a stop-cock and tube C, descending through the table to a distance of 900 mm. below the joint. It is advisable to place washers of leather at the end of the plugs of the stop-cocks *c* and *b*, as the pressure of the mercury which is to be afterwards introduced has a tendency to force them out; if this should happen, the washers prevent any great escape of mercury.

The two tubes are firmly held by a clamp D, on which rests a wide cylinder E, about 55 mm. in diameter, surrounding the tubes, and adapted to them by a water-tight caoutchouc stopper F. The cylinder is maintained in an upright position by a support at its upper end G, sliding on the same rod as the clamp. Around the upper part of the barometer tube a siphon H is fixed by means of a perforated cork, through which the stop-cock *d* passes. A small bulb-tube *e*, containing some mercury, is also fitted in this cork, so as to allow of the air being entirely removed from the

* *J. C. S.* [N.S.] 7, 313.

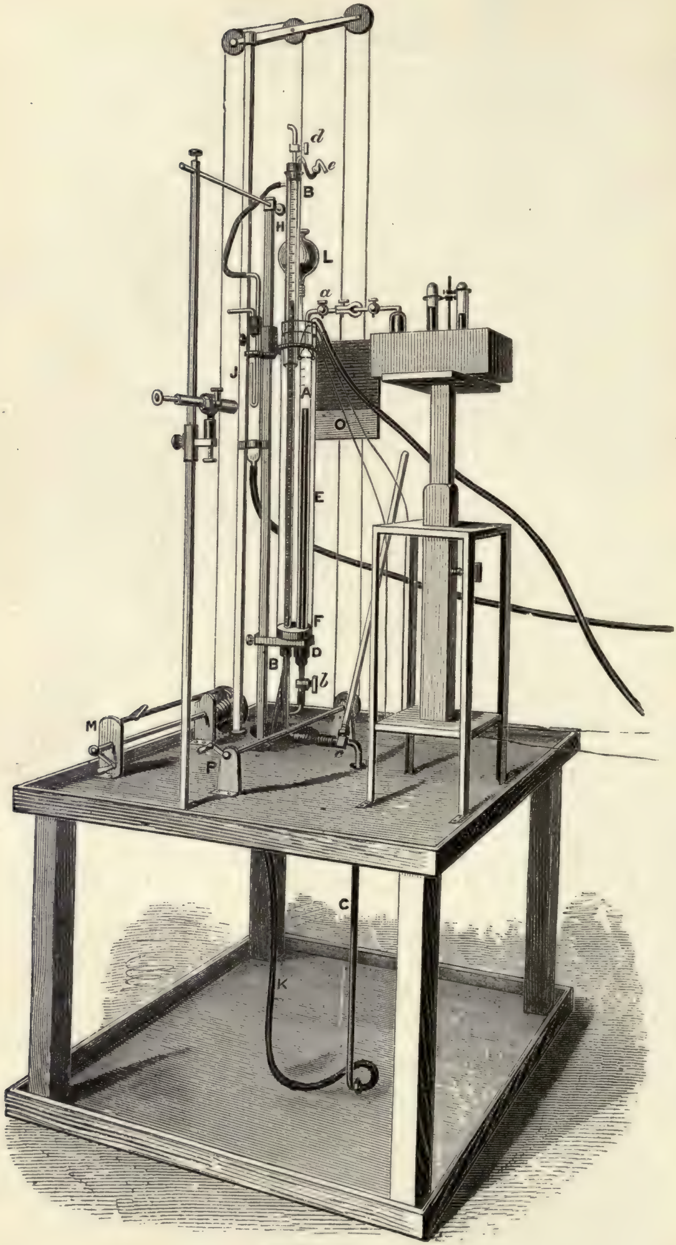


Fig. 101.

siphon. The siphon descends about 100 mm. within the cylinder, and has a branch at the top communicating by caoutchouc with a bent tube contained in a wider one J affixed to the support. A constant current of water is supplied to the cylinder through a glass tube, which passes to the bottom, and escapes through the siphon and tubes to the drain.

To the end of the narrow tube C is fastened a long piece of caoutchouc tube K, covered with tape, by which a communication is established with the mercurial reservoir L, suspended by a cord so that by means of the winch M, it may be raised above the level of the top of the barometer tube. As the mercury frequently forces its way through the pores of the caoutchouc tube, it is advisable to surround the lower part with a piece of wide flexible tube; this prevents the scattering of the mercury, which collects in a tray placed on the floor. Into the bottom of the tray a screw must be put, to which the end of the glass tube is firmly attached by wire. The capillary stop-cock *a* is provided with a steel cap, by means of which it may be adapted to a short and wide laboratory tube capable of holding about 150 c.c., and identical in form with the one described in the section on Water Analysis (p. 456). The mercurial trough for the laboratory tube is provided with a stand with rings, for the purpose of holding two tubes containing gases that may be required.

The apparatus is used in the same way as Frankland and Ward's, except that the mercury is raised and lowered in the tubes by the movement in the reservoir L, instead of by pouring it into the centre supply tube.

To arrange the apparatus for use, the reservoir L is lowered to the ground, and mercury poured into it. The laboratory tube being removed, the stop-cocks are all opened, and the reservoir gradually raised. When the tube A is filled, the stop-cock *a* is closed, and the reservoir elevated until mercury flows through the stop-cock *d* at the top of the barometer. It is convenient to have the end of the tube above the stop-cock so bent that a vessel can be placed below to receive the mercury. This bend must, of course, be so short that, when the plug of the stop-cock is removed, the siphon will pass readily over. When the air is expelled from the barometer tube, the stop-cock is closed. A few drops of water must next be introduced into the barometer; this is accomplished by lowering the reservoir to a short distance below the top of the barometer, and gently opening the stop-cock *d*, while a small pipette, from which water is dropping, is held against the orifice, the stop-cock being closed when a sufficient amount of water has penetrated into the tube. In the same manner, a small quantity of water is passed into the measuring tube. In order to get rid of any bubbles of air which may still linger in the tubes, the reservoir is lowered to the ground so as to produce a vacuum in the apparatus; in this manner the interior surfaces of the tubes become moistened. The reservoir is now gently raised, thus refilling the tubes with mercury. Great

care must be taken that the mercury does not rush suddenly against the tops of the measuring and barometer tubes, which might cause their destruction. This may be avoided by regulating the flow of mercury by means of the stop-cock *c*, which may be conveniently turned by a long key of wood, resting against the upper table of the sliding stand of the mercurial trough. When the reservoir has again been elevated above the top of the barometer, the stop-cocks of the measuring and barometer tubes are opened, and the air and water which have collected allowed to escape.

The heights of the mercurial columns in the barometer, corresponding to the different divisions of the measuring tube, have now to be determined. This is done by running out all the mercury from the tubes, and slowly readmitting it until the meniscus of the mercury just touches the lowest division in the measuring tube. This may be very conveniently managed by observing the division through a small telescope of short focus, and sufficiently close to the apparatus to permit of the key of the stop-cock *c* being turned, while the eye is still at the telescope. When a reading is taken, the black screen O behind the apparatus must be moved by means of the winch P, until its lower edge is about a millimetre above the division. The telescope is now directed to the barometer tube, and the position of the mercury carefully noted. As the tubes only contain aqueous vapour, and are both of the same temperature, the columns in the two tubes are those which exactly counterbalance one another, and any difference of level that may be noticed is due to capillarity.

The same operation is now repeated at each division of the tube. The measuring tube next requires calibration, an operation performed in a manner perfectly similar to that described on p. 457, namely, by filling the measuring tube with water, and weighing the quantities contained between every two divisions. The eudiometer being filled with water, and the stop-cock *b* closed, the reservoir is raised and the mercury allowed to rise to the top of the barometer. The capillary stop-cock *a* having been opened, the cock *b* is gently turned, and the water allowed to flow out until the mercury reaches the lowest division of the tube. A carefully weighed flask is now supported just below the steel cap, the stop-cock *b* again opened, until the next division is reached, and the quantity of water is weighed, the temperature of the water in the wide cylinder being observed. The same operation is repeated at each division, and by calculation the exact contents of the tube in cubic centimetres may be found.

In this manner, a table, such as the following, is obtained :—

Division on measuring tube.	Height of Mercury in Barometer tube corresponding to division.	Contents.	
		Cubic Centimetres.	Log.
1	756·9	8·689	0·93898
2	706·7	18·162	1·25917
3	606·8	36·931	1·56739
4	506·5	55·734	1·74612
5	406·8	74·430	1·87175
6	306·8	93·331	1·97002
7	206·9	112·417	2·05083
8	107·0	131·634	2·11937
9	7·1	151·162	2·17944

When a gas is to be analyzed, the laboratory tube is filled with mercury, either by sucking the air out through the capillary stop-cock while the open end of the tube stands in the trough, or, much more conveniently, by exhausting the air through a piece of flexible tube passed under the mercury to the top of the laboratory tube, the small quantity of air remaining in the stop-cock and at the top of the wide tube being afterwards very readily withdrawn. The face of one of the steel pieces is greased with a small quantity of resin cerate, and, the measuring apparatus being full of mercury, the clamp is adjusted.

Before the introduction of the gas, it is advisable to ascertain if the capillary tubes are clear, as a stoppage may arise from the admission of a small quantity of grease into one of them. For this purpose the globe L is raised above the level of the top of the measuring tube, and the capillary stop-cocks opened; if a free passage exists, the mercury will be seen to flow through the tubes. The stop-cock of the laboratory tube is now closed. When all is properly arranged, the gas is transferred into the laboratory tube, and the stop-cock opened, admitting a stream of mercury. The cock *c* is gently turned, so as just to arrest the flow of mercury through the apparatus, and the reservoir lowered to about the level of the table, which is usually sufficient. By carefully opening the cock *c*, the gas is drawn over into the measuring tube, and when the mercury has reached a point in the capillary tube of the laboratory tube, about midway between the bend and the stop-cock, the latter is quickly closed. It is necessary that this stop-cock should be very perfect. This is attained by grinding the plug into the socket with fine levigated rouge and solution of sodium or potassium hydrate. By this means the plug and socket may be polished so that a very small quantity of resin cerate and a drop of oil renders it perfectly gas-tight. In grinding, care must be taken that the operation is not carried on too long, otherwise the

hole in the plug may not coincide with the tubes. If this stop-cock is in sufficiently good order, it is unnecessary to close the stop-cock *a* during an analysis.

The mercury is allowed to flow out of the apparatus until its surface is a short distance below the division at which the measurements are to be taken. The selection of the division depends on the quantity of gas and the kind of experiment to be performed with it. A saving of calculation is effected if all the measurements in one analysis are carried on at the same division. When the mercury has descended below the division, the cock *c* is closed, the reservoir raised, and the black screen moved until its lower edge is about a millimetre above the division, and the telescope so placed that the image of the division coincides with the cross-wires in the eye-piece. The stop-cock *c* is now gently opened until the meniscus just touches the division; the cock is closed and the height of the mercury in the barometer is measured by means of the telescope. The difference between the reading of the barometer and the number in the table corresponding to the division at which the measurement is taken, gives in millimetres the tension of the gas. The volume of the gas is found in the same table, and with the temperature which is read off at the same time as the pressure, all the data required for the calculation of the volume of the gas at 0° and 760 mm. are obtained. No correction is required for tension of aqueous vapour; the measuring tube and barometer tube being both moist, the tensions in the tubes are counterbalanced. Absorptions are performed with liquid reagents by introducing a few drops of the liquid into the laboratory tube, transferring the gas into it, and allowing the mercury to drop slowly through the gas for about five minutes. The gas is then passed over into the measuring tube, and the difference of tension observed corresponds to the amount of gas absorbed. It is scarcely necessary to add that the greatest care must be taken to prevent any trace of the reagent passing the stop-cock. If such an accident should occur, the measuring tube must be washed out several times with distilled water at the conclusion of the analysis. If the reagent is a solution of potassium hydrate it may be got rid of by introducing into the tube some distilled water, to which a drop of sulphuric acid has been added. If this liquid is found to be acid on removing it from the tube, it may be presumed that all the alkali has been neutralized.

When explosions are to be performed in the apparatus, the gas is first measured and then returned to the laboratory tube. A quantity of oxygen or hydrogen, as the case may be, which is judged to be the proper volume, is transferred into the laboratory tube, and some mercury is allowed to stream through the gases so as to mix them thoroughly. The mixture is next passed into the eudiometer and measured. If a sufficient quantity of the second gas has not been added, more can readily be introduced. After the measurement, it may be advisable to expand the mixture, in order to diminish the

force of the explosion. This is done by allowing mercury to flow out from the tube into the reservoir. When the proper amount of expansion has been reached, the stop-cocks *a* and *b* are closed. To enable the electric spark to pass between the wires, it is necessary to lower the level of the water in the cylinder. For this purpose, the bent glass tube at the extremity of the siphon is made to slide easily through the cork which closes the top of the wide tube J. By depressing the bent tube, the water flows out more rapidly than before, and the level consequently falls. When the surface is below the eudiometer wires, a spark from an induction-coil is passed, exploding the gas. The siphon tube is immediately raised, and, when the water in the cylinder has reached its original level, the gas is cool enough for measurement. 900 c.c. of mercury are amply sufficient for the whole apparatus ; and as there is no cement used to fasten the wide tubes into iron sockets, a great difficulty in the original apparatus is avoided.

The following details of an analysis, in which absorptions only were performed, will show the method employed. The gas was a mixture of nitrogen, oxygen, and carbonic anhydride, and the measurements were all made at division No. 1 on the eudiometer, which has been found to contain 8·6892 c.c.

Original Gas.

The absorbing liquids required are :—

For carbon dioxide : a solution of caustic potash of sp. gr. 1·20.

For oxygen : the same solution, to which some saturated solution of pyrogallol is added.

Temperature of water in cylinder, 15·4°.	mm.
Height of mercury in barometer tube	980·5
,, ,, corresponding to Division No. 1 (see Table)	756·9
Pressure of the gas	223·6
After absorption of the carbonic anhydride by solution of potassium hydrate—	
Height of mercury in barometer tube	941·7
,, ,, corresponding to Division No. 1 .	756·9
Pressure of the gas after removal of carbonic anhydride .	184·8
Pressure of original gas	223·6
,, gas after removal of carbonic anhydride . .	184·8
Tension of carbonic anhydride	38·8
After absorption of the oxygen by potassium pyrogallate—	
Height of mercury in barometer tube	885·4
,, ,, corresponding to Division No. 1 .	756·9
Pressure of nitrogen	128·5
Pressure of oxygen and nitrogen	184·8
,, nitrogen	128·5
,, oxygen	56·3

These measurements, therefore, give us the following numbers :—

	mm.
Pressure of nitrogen	128·5
,, oxygen	56·3
,, carbonic anhydride	38·8
,, original gas	223·6

If the percentage composition of the gas is required, it is readily obtained by a simple proportion, the temperature having remained constant during the experiment :—

$$223·6 : 128·5 :: 100 : 57·47 \text{ per cent. N}$$
$$223·6 : 56·3 :: 100 : 25·18 \text{ per cent. O}$$
$$223·6 : 38·8 :: 100 : 17·35 \text{ per cent. } CO_2$$
$$100·00$$

If, however, it is necessary to calculate the number of cubic centimetres of the gases at 0° and 760 mm., it is done by the following formulæ :—

$$\frac{8·6892 \times 128·5}{760 \times [1 + (0·003665 \times 15·4)]} = 1·39 \text{ c.c. of nitrogen.}$$

$$\frac{8·6892 \times 56·3}{760 \times [1 + (0·003665 \times 15·4)]} = 0·61 \text{ c.c. of oxygen.}$$

$$\frac{8·6892 \times 38·8}{760 \times [1 + (0·003665 \times 15·4)]} = 0·42 \text{ c.c. of carbonic anhydride.}$$

$$\frac{8·6892 \times 223·6}{760 \times [1 + (0·003665 \times 15·4)]} = 2·42 \text{ c.c. of the original gas.}$$

If many of the calculations are to be done, they may be very much simplified by constructing a table containing the logarithms of the quotients obtained by dividing the contents of each division of the tube by $760 \times (1 + 0·003665t)$. The following is a very short extract from such a table :—

T°.	Division No. 1. Log. $\frac{8·6892}{760 \times (1+\delta t)}$.	Division No. 2. Log. $\frac{18·1621}{760 \times (1+\delta t)}$.
15·0	$\bar{2}·03492$	$\bar{2}·35511$
·1	$\bar{2}·03477$	$\bar{2}·35496$
·2	$\bar{2}·03462$	$\bar{2}·35481$
·3	$\bar{2}·03447$	$\bar{2}·35466$
·4	$\bar{2}·03432$	$\bar{2}·34451$

By adding the logarithms of the tensions of the gases to those in the above table, the logarithms of the quantities of gases are obtained ; thus :—

Log. corresponding to Division No. 1, and 15·4°	$\bar{2}$·03432
Log. 128·5 = pressure of nitrogen .	2·10890
Log. of quantity of nitrogen . .	0·14322 = log. 1·39
Volume of nitrogen at 0° and 760 mm.	1·39 c.c.
	$\bar{2}$·03432 :
Log. 56·3 = pressure of oxygen .	$\bar{1}$·75051
Log. of quantity of oxygen . .	$\bar{1}$·78483 = log. 0·61
Volume of oxygen at 0° and 760 mm.	0·61 c.c.
	$\bar{2}$·03432
Log. 38·8 = pressure of carbonic anhydride	$\bar{1}$·58883
Log. of quantity of carbonic anhydride	$\bar{1}$·62315 = log. 0·42
Volume of carbonic anhydride at 0° and 760 mm.	0·42 c.c.
	$\bar{2}$·03432
Log. 223·6 = pressure of original gas	2·34947
Log. of quantity of original gas .	0·38379 = log. 2·42
Volume of original gas at 0° and 780 mm.	2·42 c.c.
Nitrogen	1·39 c.c.
Oxygen	0·61 c.c.
Carbonic anhydride . . .	0·42 c.c.
Total	2·42 c.c.

The following example of an analysis of coal gas will show the mode of working with this apparatus, and the various operations to be performed in order to determine the carbonic anhydride, oxygen, hydrocarbons absorbed by Nordhausen sulphuric acid, hydrogen, methane, carbonic oxide, and nitrogen.

The measuring tube and laboratory tube were first filled with mercury, some of the gas introduced into the laboratory tube, and passed into the apparatus.

The gas was measured at the second division.

Height of mercury in the barometer tube . .	989·0
,, ,, ,, measuring tube . .	706·8
Pressure of the gas at 16·6°	282·2

Two or three drops of a solution of potassium hydrate were now placed in the laboratory tube, and the gas passed from the measuring tube, the mercury being allowed to drop through the gas for ten minutes. On measuring again—

Height of mercury in barometer	984·0

Some saturated solution of pyrogallic acid was introduced into the laboratory tube, and the gas left in contact with the liquid for ten minutes. On measuring—

Height of mercury in barometer	. . . . .	983·6
Height of mercury when measuring original gas	.	989·0
,, ,,	after absorption of CO_2 .	984·0
	Pressure of CO_2	5·0
,, ,,	after absorption of CO_2 .	884·0
,, ,,	after absorption of O .	983·6
	Pressure of O	0·4

The volumes of the gases being proportional to their pressures, it is a simple matter to obtain the percentages of carbonic anhydride and oxygen in the original gas.

Original gas.		CO_2				
282·2	:	5·0	: :	100	:	1·77 per cent. CO_2
Original gas.		O				
282·2	:	0·4	: :	100	:	0·14 per cent. O
						1·91

By subtracting 1·91 from 100, we obtain the remainder, 98·09, consisting of the hydrocarbons absorbed by Nordhausen sulphuric acid, hydrogen, carbonic oxide, marsh gas, and nitrogen; thus:—

Original gas	100·00
O and CO_2	1·91
C_nH_{2n}. H_2. CO. CH_4. N_2.	98·09

While the gas remains in the measuring tube, the laboratory tube is removed, washed, dried, filled with mercury, and again attached to the apparatus. Much time is saved by replacing the laboratory tube by a second, which was previously ready. As a minute quantity of gas is lost in this operation, in consequence of the amount between the stop-cocks being replaced by mercury, it is advisable to pass the gas into the laboratory tube, then transfer it to the eudiometer, and measure again.

On remeasuring, the mercury in the barometer stood at	983·3
The mercury in the measuring tube . . .	706·8
Pressure of C_nH_{2n}. H_2. CO. CH_4. N_2.	276·5

The gas is again passed into the laboratory tube, and a coke ball, soaked in fuming sulphuric acid, left in contact with the gas for an hour; the bullet is then withdrawn, and some potassium hydrate introduced and left in the tube for ten minutes, in order to remove the vapours of sulphuric anhydride, and the sulphurous and carbonic anhydrides formed during the action of the Nordhausen acid on the gas. The gas is now measured again.

Height of mercury in barometer tube . . .	969·3
,, ,, ,, ,, before absorbing C_nH_{2n}	983·3
,, ,, ,, ,, after	969·3
Pressure of CnH_2n	14·0

The percentage of these hydrocarbons is thus found :—

Gas containing C_nH_{2n}. H_2. CO. CH_4. N_2.

276·5 : 14·0 : : 98·09 : 4·97 per cent. C_nH_{2n}.

It now remains to determine the hydrogen, carbonic oxide, methane, and nitrogen in a portion of the residual gas. The laboratory tube is therefore removed, some of the gas allowed to escape, and another laboratory tube adapted to the apparatus. The portion of gas remaining is expanded to a lower ring (in this special case to the third division), and the tension measured :—

Height of mercury in the barometer tube . .	642·2
,, ,, ,, measuring tube . .	606·7
Pressure of residue	35·5

An excess of oxygen has now to be added. For this purpose the gas is passed into the laboratory tube, and about five times its volume of oxygen introduced from a test tube or gas pipette. The necessary quantity of oxygen is conveniently determined by the aid of rough graduations on the laboratory tube, which are made by introducing successive quantities of air from a small tube in the manner previously described for the calibration of the eudiometers.

After the introduction of the oxygen, the mixed gases are passed into the eudiometer and measured.

Height of mercury in the eudiometer after addition of O	789·5

The mixture has now to be exploded, and when the pressure is considerable, it is advisable to expand the gas so as to moderate the violence of the explosion. When sufficiently dilated, the stop-cock at the bottom of the eudiometer is closed, the level of the water lowered beneath the platinum wires by depressing the siphon, and the spark passed. The explosion should be so powerful that it should be audible, and the flash visible in not too bright daylight.

The stop-cock at the bottom of the eudiometer is now opened, and the gas measured.

Height of mercury in barometer after explosion .	732·5

The difference between this reading and the previous one gives the contraction produced by the explosion :

Height of mercury in barometer before explosion	789·5
,, ,, ,, ,, after ,,	732·5
Contraction = C	57·0

It is now necessary to determine the amount of carbonic anhydride formed. This is done by absorbing with potassium hydrate as before described.

Height of mercury in barometer tube after absorbing CO_2	715·8

This number deducted from the last reading gives the carbonic anhydride.

Height of mercury in barometer after exploding .	732·5
,, ,, ,, ,, after absorbing CO_2	715·8
Carbonic anhydride = D	16·7

It now remains to determine the quantity of oxygen which was not consumed in the explosion, and which excess now exists mingled with the nitrogen. For this purpose, a volume of hydrogen about three times as great as that of the residual gas is added, in the same way as the oxygen was previously introduced, and the pressure of the mixture determined.

Height of mercury in barometer after adding H	1031·3

This mixture is exploded and another reading taken.

Height of mercury in barometer after exploding with H	706·7

This number subtracted from the former, and the difference divided by 3, gives the excess of oxygen.

Height of mercury in barometer before exploding with H	1031·3
Height of mercury in barometer after exploding with H	706·7
3)	324·6
Excess of oxygen	108·2

In order to obtain the quantity of nitrogen in the gas analyzed, this number has to be deducted from the volume of gas remaining after the explosion with oxygen and the removal of the carbonic anhydride.

Height of mercury in barometer after absorbing CO_2	715·8
,, ,, in eudiometer at division No. 3	606·7
Nitrogen and excess of oxygen	109·1
Excess of oxygen	108·2
Nitrogen	0·9

We have now all the data necessary for the calculation of the composition of the coal gas. It is first requisite to calculate the proportion of the combustible gas present in the coal gas, which is done by deducting the sum of the percentages of gas determined by absorption from 100.

Percentage of carbonic anhydride	. . . . .	1·77
,, oxygen	. . . .	0·14
,, $C_n H_{2n}$	. . . .	4·97
	CO_2. O_2. $C H_{2n}$	6·88
Original gas	. . . .	100·00
CO_2. O_2. $C\ H_{2n}$	. . . .	6·88
	H_2. CO. CH_4. N_2	93·12

The formulæ for the calculation of the analysis of a mixture of hydrogen, carbonic oxide, and methane, are (see page 534)—

$$\text{Hydrogen} = x = A - D$$

$$\text{Carbonic oxide} = y = \frac{3A - 2C + D}{3}$$

$$\text{Methane} = z = \frac{2C - 3A + 2D}{3}$$

$$A = 35·5 - 0·9 = 34·6$$
$$C = 57·0$$
$$D = 16·7$$

$$\begin{array}{r}
A = 34·6 \\
D = 16·7 \\
\hline
17·9
\end{array} = x = \text{Hydrogen in 35·5 of the gas exploded with oxygen.}$$

$$\begin{array}{r}
A = 34·6 \\
3 \\
\hline
3A = 103·8 \\
D = 16·7 \\
\hline
3A + D = 120·5 \\
2C = 114·0 \\
\hline
3)\ 6·5 = 3A + D - 2C
\end{array}
\qquad
\begin{array}{r}
C = 57·0 \\
2 \\
\hline
2C = 114·0
\end{array}$$

$$\frac{3A + D - 2C}{3} = 2·17 = y = \text{Carbonic oxide in 35·5 of the gas.}$$

$$\begin{array}{r}
D = 16·7 \\
2 \\
\hline
2D = 33·4 \\
2C = 114·0 \\
\hline
2D + 2C = 147·4 \\
3A = 103·8 \\
\hline
3)\ 43·6 = 2D + 2C - 3A
\end{array}$$

$$\frac{2D + 2C - 3A}{3} = 14·53 = z = \text{Methane in 35·5 of the gas.}$$

These numbers are readily transformed into percentages, thus :—

35·5 : 17·9 : : 93·12 : 46·95 per cent. of Hydrogen.
35·5 : 2·17 : : 93·12 : 5·68 per cent. of Carbonic oxide.
35·5 : 14·53 : : 93·12 : 38·12 per cent. of Methane.
35·5 : 0·9 : : 93·12 : 2·36 per cent. of Nitrogen.

This completes the calculations, the results of which are as follows :—

Hydrogen	46·95
Methane	38·12
$C_n H_{2n}$	4·97
Carbonic oxide	5·68
Carbonic anhydride	1·77
Oxygen	0·14
Nitrogen	2·36
	99·99

It is obvious that this analysis is not quite complete, since it does not give any notion of the composition of the hydrocarbons absorbed by the Nordhausen acid. To determine this, some of the original gas, after the removal of the carbonic anhydride and oxygen, is exploded with oxygen, and the contraction and carbonic anhydride produced are measured. The foregoing experiments have shown the effect due to the hydrogen, carbonic oxide, and methane, the excess obtained in the last explosion being obviously caused by the hydrocarbons dissolved by the sulphuric acid, and from these data the composition of the gas may be calculated.

It may be remarked that analyses of this kind were performed with the apparatus at the rate of two a day when working for seven hours.

It may be useful to show how this analysis appears in the laboratory note-book :

Analysis of Coal Gas.

989·0	(16·6°)	989·0	984·0	
706·8	original	984·0	983·6	
282·2	gas	5·0 = CO_2	0·4 = O	
984·0	Aft. absorb. CO_2	282·2 : 5·0 : : 100 : 1·77 CO_2		
		282·2 : 0·4 : : 100 : 0·14 O		
983·6	Aft. absorb. O		1·91	
		100·00		
983·3	Remeasured	1·91 CO_2. O		
		98·09 $C_n H_{2n}$. H. CO. CH_4. N.		
969·3	Aft. absorb. $C_n H_{2n}$	983·3	983·3	
		706·8	969·3	
		276·5	14·0 $C_n H_{2n}$	
642·2	Portion of			
606·7	Residue	276·5 : 14·0 : : 98·09 : 4·97 $C_n H_{2n}$		
35·5				
				CO_2 = 1·77
789·5	with O	35·5 = H. CO. CH_4. N.		O = 0·14
		0·9 = N		$C_n H_{2n}$ = 4·97
732·5	Aft. expl.	34·6 = H. CO. CH_4 = A		6·88

715·8 Aft. absorb. CO_2	789·5	732·5
	732·5	715·8
1031·3 with H	57·0 = contraction = C	16·7 = CO_2 = D
706·7 Aft. expl.	1031·3	715·8
	706·7	606·7
	3)324·6	109·1 = N + O
	108·2 = O	108·2 = O
		0·9 = N

$$H = x = A - D = 17{\cdot}9$$

$$CO = y = \frac{3A - 2C + D}{3} = 2{\cdot}17$$

$$CH_4 = z = \frac{2C - 3A + 2D}{3} = 14{\cdot}53$$

$$34{\cdot}60$$

34·6 = A	34·6 = A	16·7 = D
16·7 = D	3	2
17·9 = x = H	103·8 = 3A	33·4 = 2D
	16·7 = D	114·0 = 2C
57·0 = C	120·5 = 3A + D	147·4 = 2C + 2D
2	114·0 = 2C	103·8 = 3A
114·0 = 2C	3) 6·5 = 3A + D − 2C	3) 43·6 = 2D + 2C − 3A
	2·17 = y = CO	14·53 = z = CH_4

100·00	35·5 : 17·9 : : 93.12 : 46·95 H
6·88 CO. O. C_nH_{2n}	35·5 : 2·17 : : 93.12 : 5·68 CO
	35·5 : 14·53 : : 93·12 : 36·12 CH_4
93·12 H. CO. CH_4. N.	35·5 : 0·9 : : 93·12 : 2·36 N

H	=	46·95
CH_4	=	38·12
C_nH_{2n}	=	4·97
CO	=	5·68
CO_2	=	1·77
O	=	0·14
N	=	2·36
		99·99

It is assumed, in the above example, that the temperature of the water in the cylinder remained constant throughout the period occupied in performing the analysis. As this very rarely happens, the temperature should be carefully read off after every measurement of the gas and noted, in order that due correction be made for any increase or decrease of volume which may result in consequence.

THOMAS'S MODIFIED GAS APPARATUS.

In the *Chemical Society's Journal* for May, 1879, Thomas described an apparatus for gas analysis (fig. 102) which has the closed pressure tube of Frankland and Ward, and is supplied with mercury by means of the flexible rubber tube arrangement of

Mc Leod. The manner in which this apparatus is filled with mercury and got into order for working is so similar to that already described that no further reference need be made thereto.

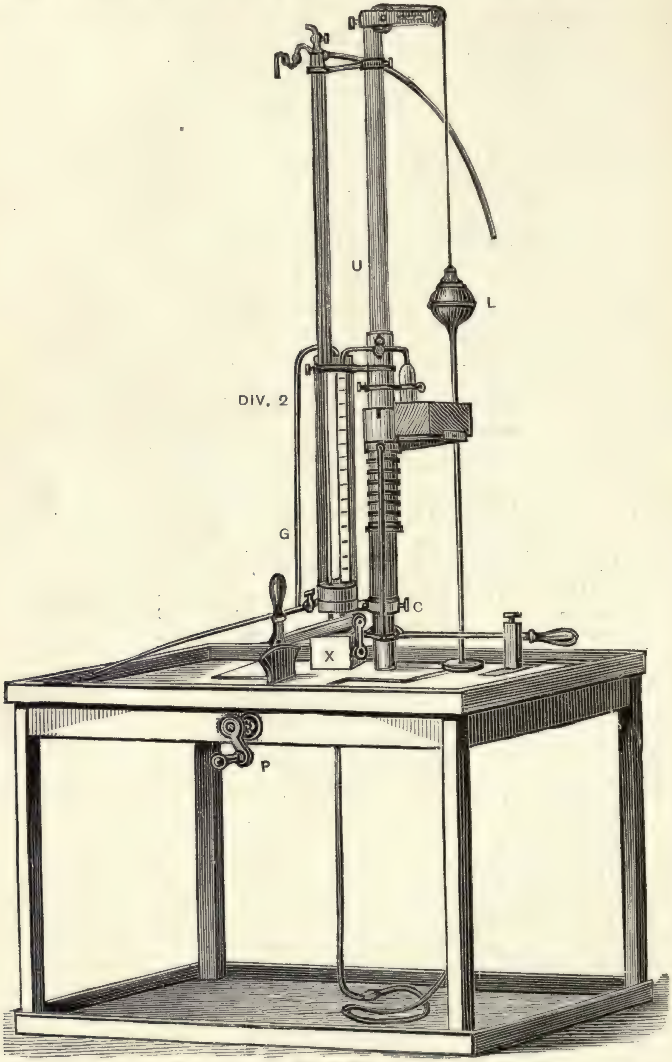


Fig. 102.

The eudiometer is only 450 mm. long from shoulder to shoulder, and the laboratory tube and mercury trough are under the command of the operator from the floor level. The eudiometer has divisions 20 mm. apart, excepting the uppermost, which is placed as close beneath the platinum wires as is convenient to obtain a reading.

The method explained in sequel of exploding combustible gases under reduced pressure, without adding excess of gas to modify the force of the explosion, permits the shortening of the eudiometer as above, and enables the apparatus to be so erected that a long column of the barometer tube shall stand above the summit of the eudiometer. By means of such an arrangement a volume of gas may be measured under nearly atmospheric pressure, and as this pressure is equal to more than 700 mm., plus tension of aqueous vapour, the sensitiveness of the apparatus is considerably augmented. The barometer tube is 1000 mm. in length, having about 700 mm. lines above Division 2 on the eudiometer. The steel clamp and facets forming the connections between the eudiometer and detachable laboratory tube of the apparatus previously described are dispensed with, as in this form the eudiometer and laboratory vessels are united by a continuous capillary tube, 12 mm. (outside) diameter, and one three-way glass tap is employed in lieu of the two stop-cocks. The arrangement is simple. The glass tap is hollow in the centre, and through this hollow a communication is made with the capillary, by means of which either the laboratory tube or the eudiometer can be washed out. As the laboratory vessel is not disconnected for the removal of the reagent used in an absorption, it is supported by a clamp, as shown in the drawing; and when it requires washing out the mercury trough is turned aside in order that an enema syringe may be used for injecting a stream of water. A few drops of water are let fall into the hollow of the tap, and blown through the capillary tube three times in succession, so as to get rid of the absorbent remaining in the capillary, then the syringe is brought into play once more, the excess of water removed by wiping, and the trough turned back into position. The laboratory tube may be refilled with mercury, as described on page 549, but it will be found much more serviceable if a double-acting syringe, connected to a bulb apparatus (to catch any mercury that may come over), and then to the orifice of the hollow in the tap by a ground perforated stopper, be used, as this will obviate the destructive effect of heavy suction upon the gums and teeth. The mercury trough is supported upon a guide which travels over the upright U, and is turned aside for the purpose of washing out the laboratory vessel in the following manner :—The spiral spring is depressed by means of the tension rods until the slot is brought below the stud fixed in the upright U; and the top ferrule holding the guide rods being movable, the trough can be turned round out of the way, but is prevented from coming in contact with the glass water-cylinder by an arrangement in the top of the guide, which comes against the stud in the upright. The height of the trough can be accurately adjusted by the screw in the top of the lever guide. When the trough is in position, the clamp holding the laboratory vessel may be loosed when necessary.

The eudiometer and barometer tubes pass through an india-rubber stopper, as in Mc Leod's apparatus, but are not supported

by the clamp C, which here simply bears the water-cylinder. No glass stop-cocks are used, or glass work of any kind employed in the construction of the lower portion of the apparatus. The lower end of the eudiometer has a neck of the same outside diameter as the barometer tube (9·5 mm.), and both tubes are fixed into the steel block X, without rigidity, by the usual steam cylinder gland arrangement, small india-rubber rings being used to form the packing. The steel block is fixed to the table by a nut screwed upon the $\frac{3}{8}$-inch hydraulic iron tube, which runs to the bottom of the table. The tap in the steel block is so devised that it first cuts off connection with the barometer tube, in order that the gas may be drawn over from the laboratory vessel into the eudiometer without risking the fracture of the upper end of the barometer tube by any sudden action of the mercury. This precaution is necessary, as during the transferring of the gas the mercury in the barometer tube is on the point of lowering, to leave a vacuous space in the summit of the tube. By moving the handle a little further on the quadrant a communication is made with both tubes and the reservoir for the purpose of bringing the gas into position, so as to take a reading; then the handle is drawn a little further to cut off the reservoir supply, whilst there is a way still left between the eudiometer and barometer tubes, and if the handle be drawn forward a little more, all communication is cut off for the purpose of exploding.

The windlass P, for raising and lowering the mercury reservoir L, is placed beneath the table, in order that it may be under command from a position opposite the laboratory vessel, and it is furnished with a spring ratchet motion, so as to be worked by one hand. The water-cylinder should be four inches in diameter, and the casing tube of the barometer as wide as practicable, so that the temperature of the apparatus may be maintained as constant as possible. To attain an accurate result it is as essential to keep the barometer tube of uniform temperature as the eudiometer, since the tension of aqueous vapour varies proportionately. The stream of water from the service main is run into the casing tube at the upper end of the barometer, and, whilst the water-cylinder is filling, the tap at the bottom is opened slightly, so that water may run out very slowly. When the water-cylinder is full, the upright tube G acts as a siphon, and sucks out the excess of water from the top of the cylinder, thus keeping up the circulation at the point where it is most required. For a further detailed description of the apparatus see *J. C. S.*, May, 1879.

There are only two working taps upon this apparatus—the three-way glass tap between the eudiometer and laboratory tube, and the steel cap at the lower ends of the barometer and eudiometer. The steel cap is greased with a little beef-tallow (made from clean beef-suet), or with real Russian tallow; it will last for twelve months without further attention. A moderately thick washer of india-rubber, placed between the steel washer and the nut at the end of the steel tap, adds greatly to the steady working of the needle on

the quadrant. Moderately soft resin cerate is best for the glass tap.

When filling the laboratory vessel with mercury, suction is maintained until the mercury has reached some height in the hollow of the three-way tap. The remainder of the hollow space is replenished by pouring the mercury from a small crucible ; any water that may be present is then removed, and the small stopper inserted. When the laboratory vessel has to be washed out after an absorption, the gas is transferred to the eudiometer until the absorbent gets within a quarter of an inch of the stop-cock. The mechanical arrangement should be so manageable that this nicety of adjustment can be accomplished with ease. Much depends, of course, upon the care bestowed in cerating the tap, so that the capillary is not carelessly blocked up. As soon as the gas has passed over to the extent required, turn the three-way tap until the through-way is at right-angles to the capillary, and the way to the hollow of the tap is in communication with the laboratory vessel, then take out the little stopper from the hollow, so that the mercury shall flow out, and allow the laboratory vessel to become emptied whilst the reading of the volume of the gas is being taken. The best arrangement for washing out the laboratory tube is a "siphon enema," fig. 103 (Dr. Higginson's principle, which may be obtained of any druggist), adapting in the place of the usual nozzle a bent glass tube. This syringe is constant in its action, as it fills itself when the pressure is released, if the tube at the lower end is placed in a vessel of water. The laboratory vessel can be washed out and refilled in a very little time, as it is already connected, and for all ordinary absorptions it is sufficient to wipe the vessel out once by passing up a fine towel twisted on a round stick. When $C_n H_{2n}$ gases are to be absorbed by fuming sulphuric acid, the water should be carefully blown out of the capillary tube into the laboratory vessel, which must be repeatedly dried. A few drops of strong sulphuric acid were at first run into the hollow of the tap and then through the capillary whilst the laboratory vessel was full of mercury, in order to remove any moisture remaining, but it has since been found unnecessary, as the drying can be performed thoroughly without.

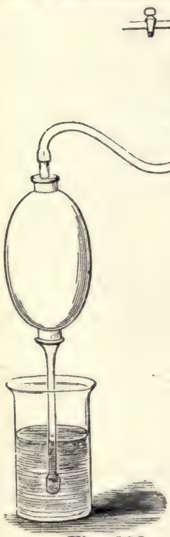


Fig. 103.

To calibrate the eudiometer with water, introduce the quantity required through the hollow in the stopper, then remove the latter, and collect the water in a light flask from the bottom of the tap-socket.

In the same paper (*J. C. S.*, May, 1879), Thomas pointed out that it was not essential to add excess of either oxygen or hydrogen for the purpose

of modifying the force of the explosion when combustible gases were under analysis, and it is necessary to take advantage of this when working with so short an eudiometer. The method is, however, applicable to all gas apparatus having a reasonable length of barometer column above the eudiometer; in fact, the exploding pressures were first worked out and employed in an apparatus on Mc Leod's model. When the percentage of oxygen in a sample of air has to be determined by explosion, only one-half its volume of hydrogen is required, and the pressure need not be reduced below 400 mm. If much more than one-half volume of hydrogen has been added by accident, explode under atmospheric pressure. When the excess of oxygen used in an analysis has to be determined, add 2·5 times its volume of hydrogen, and reduce the pressure to 180 mm. of mercury before exploding. After adding the hydrogen and taking the reading, the gas is expanded by lowering the mercurial reservoir until a column of mercury, measuring the number of mm. in length just referred to and in the following table, stands above the meniscus of the mercury in the eudiometer. This column can be read off quite near enough by the eye, as there is no risk of breaking the apparatus by the force of the explosion if the pressure is 20 mm. greater than that given; but if the gas under analysis is all combustible, it is better to explode at a slightly less pressure than to exceed that recommended. It follows, naturally,

Name of Gas.	Volume of Combustible Gas.	Volume of Oxygen to be added.	Pressure of mixture before exploding.
Hydrogen	1	1	200 mm.
Carbonic Oxide	1	1	200 mm.
Methane	1	2·5	170 mm.
Acetylene	1	3	150 mm.
Ethylene	1	3·5	145 mm.
Ethane and Hydride of Ethyl	1	4	140 mm.
Propyl	1	5	135 mm.
Hydride of Propyl	1	5·5	130 mm.
Butyl	1	6	125 mm.
Butane and Hydride of Butyl	1	7	120 mm.

that the exploding pressure will depend upon the proportion of combustible gas introduced; and experience alone can enable one to determine with any degree of exactness what that pressure must be, as no general law can be laid down. For instance, if more than three volumes of hydrogen were added to one of oxygen, the exploding pressure should exceed 200 mm.; and if much nitrogen or other gas were present that did not take a part in the reaction, the pressure should be still more increased. As a consequence, the

same experience is necessary when dealing with explosive gases by the other method, because the addition of too much inert gas, with a view to modify the force of the explosion, may lead to imperfect combustion, inasmuch as the cooling effect of the tube and gas can reduce the temperature below that required. In all instances, when the approximate composition of the gas is known, it is not difficult to determine the quantity of oxygen or hydrogen, as the case may be, which is required for explosion, or the pressure under which the gas should be exploded. In order to do this systematically, it is always well to remember certain points observed during the stages of the analysis. The gas in the laboratory vessel, before being transferred to the eudiometer, occupies a certain volume in a position between (or otherwise) the calibration divisions. After transferring and reading off, bear in mind the number of millimetres which the volume represents ; and calculate, as the gas is being re-transferred to the laboratory vessel to be mixed with that employed in the explosion, the height at which the mercury should stand in the barometer tube when measuring the mixed gases, and how much of the laboratory vessel was occupied on a previous occasion when a similar reading was obtained. If this is done, one can realize at once, after reading off the volume of the mixed gases, the proportion of combustible gas added, and the pressure under which the gas has been measured. Another glance at the volume which the gas occupies in the eudiometer, with a comparison of the pressure recorded upon the barometer tube, enables one, after a little practice, at once to expand the mixture to the point at which it will explode with satisfactory results. It is not expedient to place too much reliance upon the marks showing equal volumes upon the laboratory vessel, especially when dealing with small quantities of gas ; and a comparison of the volumes obtained in reading before and after the addition of oxygen or hydrogen is always prudent, in order to see that sufficient gas has been added, as well as to enable one to judge the pressure under which the gas should be exploded.

NOTE.—Meyer and Seubert (*Z. a. C.* **24**, 414) have designed a gas apparatus similar in many respects to that of McLeod and Thomas, but of simpler construction, and especially adapted for explosions under diminished pressure.

SODEAU'S GAS APPARATUS.

This form of instrument is shown in fig. 104, and is described in a paper read by W. H. Sodeau before the Newcastle Section of the Society of Chemical Industry, and is printed in full in the journal of that Society (xxii. 187). It is an improved form of an instrument previously devised by Macfarlane and Caldwell, and in its present state is adapted for gas analysis of the highest accuracy.* In addition to this, its cost is much less than most of those which have been previously described.

* Brady and Martin of Newcastle-on-Tyne are the original makers.

Description of the Apparatus.—The measuring parts are fitted into a glass water jacket, which is held in position by means of a cork at A and a band-clip at B. The measuring tube M is of 50 c.c. capacity graduated in $\frac{1}{10}$ c.c. Its upper end terminates in a capillary bearing a three-way stop-cock. When examining samples which leave a large residue after absorption, etc., it is convenient to replace the usual tube of uniform diameter by one having a bulb at its upper end. The zero-point is at the outer side

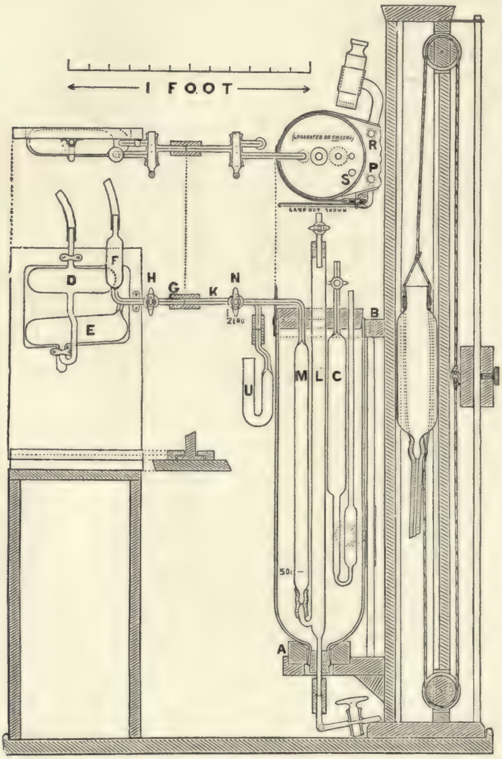


Fig. 104.

of the three-way stop-cock N, which is placed horizontally. The bent tube U, partly filled with water, can be connected with the capillary K through the stop-cock. The level tube L is straight, with stop-cock at top, and communicates with the measuring tube by a branch so bent as to prevent any bubbles rising from below from passing into the measuring tube. The lower end is connected to a T piece, one end of which has a stop-cock and leads to the mercury reservoir, and the other is prolonged across the table to a point near the reading telescope, where it terminates in a thick piece of rubber tubing compressed by a screw clip having a broad

bearing surface. This is used as a fine adjustment when levelling the mercury. The graduations are on the side next the telescope, and the stop-cocks are worked from the opposite side. This arrangement renders it possible to have the reading telescope on the gas analysis table instead of on a separate support, and so adds to the compactness and convenience of the apparatus. The graduations can be illuminated by an electric lamp behind a ground glass screen, having its upper portions rendered opaque in order to prevent troublesome reflection of light from the surface of the mercury.

Correction for variation of temperature and pressure is simplified by the use of the "Kew principle" correction tube C. This consists of a cylindrical bulb provided with a stop-cock and attached to a U tube graduated on the narrow limb and partially filled with water. The volume of air contained in the bulb is such that the water is displaced to the extent of one small division by a change of temperature and atmospheric pressure which will cause a gas to experience an alteration of volume amounting to 0·1 per cent.* The scale is observed by means of a mounted lens and the small divisions are further sub-divided into tenths by eye estimation. The water is brought approximately to the zero mark at the beginning of an analysis by momentarily opening the stop-cock, and the corrections are read directly in percentages as easily as the temperatures would be read by means of a thermometer.

METHOD OF PROCEDURE: Introduce the gas into the measuring tube M by lowering the reservoir. Roughly level the mercury and turn the stop-cock N so as to connect K with the tube U. Place the absorption pipette in position and connect it to the measuring apparatus by thick-walled rubber tubing, the glass ends being made to meet.

Suck a little water from U into F, and allow mercury to run back and fill the capillaries.

Let the capacity of the bulb, together with that of the portion of the tube which is above the zero point = X c.c., and assume the atmospheric pressure to be 760 mm. Then if a change which would lead to a 1 per cent. increase of volume is to give 0·5 c.c. displacement of water, and this results in a disturbance of level amounting to N mm., it follows that

$$1{\cdot}01\ X = (X + 0{\cdot}5)\left(1 + \frac{N}{760 \times 13{\cdot}5}\right) \therefore X = \frac{10{\cdot}260 + N}{205{\cdot}2 - 2N}$$

No appreciable error is likely to be introduced by the atmospheric pressure markedly deviating from the value assumed in this calculation.

If the internal diameters of the two limbs of the U tube are d_1 mm. and d_2 mm. respectively, then

$$N = \frac{636{\cdot}6}{d_1^2} + \frac{636{\cdot}6}{d_2^2} \text{ and } X = \frac{50 d_1^2\, d_2^2 + 3{\cdot}1\ (d_1^2 + d_2^2)}{d_1^2\, d_2^2 - 6{\cdot}2(d_1^2 + d_2^2)}$$

EXAMPLE.—If $d_1 = 6{\cdot}9$ mm. and $d_2 = 15{\cdot}5$ mm., then $N = 13{\cdot}35 + 2{\cdot}65 = 16{\cdot}0$ and $X = 59{\cdot}4$ c.c.

Next close the stop-cock leading to the large mercury reservoir, make sure

* The Absorption Pipette differs from that of Macfarlane and Caldwell in two important points. First, the lower bulb E, of about 80 c.c. capacity, is inclined so that the unabsorbed gas may readily be returned to the measuring vessel without tilting the whole apparatus. Second, the connection is made by means of a three-way stop-cock so that the capillary G may be connected either with E containing the absorbent over mercury or with F containing clean mercury. The ends of the capillaries G and K must be free from appreciable unevenness. It is important that the bore of these tubes should neither exceed 1·5 mm. nor be less than 1 mm., and their external diameter should be about 6 mm.

that the level tube is in free communication with the atmosphere, and level accurately by means of the screw clip, which acts as a fine adjustment and which should be alongside the reading telescope. Finally, read the correction tube. It is convenient to enter the readings thus :—

Correction.	Reading.	Corrected Reading.
+0·04 per cent.	49·97 c.c.	49·99 c.c.

The gas is next sent over into the absorption pipette, followed by sufficient mercury to clear the capillaries, and the pipette shaken with the stop-cock closed until absorption is complete. Run over a little more mercury in order to clear absorbent from the capillary between E and H. Send the soiled mercury in the capillaries into U. When the gas reaches N turn the stop-cock and run it into the measuring tube, controlling the rate by H. The absorbent is readily stopped when it reaches H and the capillary is cleared of gas by means of clean mercury from F, this being stopped as soon as it reaches N. It is advisable to turn the stop-cock N so as to place K in communication with U whilst removing a pipette. By means of a retort stand a small evaporating basin may be supported about 2 inches below G in order to catch drops of mercury.

If, as in the determination of carbon monoxide, it is necessary to subject the gas to more than one treatment with an absorbent, the first pipette is brought into direct connection with the second and the gas transferred. With fuming sulphuric acid as an absorbent, no mercury is used in E, a U tube with pumice and strong sulphuric acid is attached to D to prevent access of moisture, and the mercury from the capillaries is driven into F. The explosion pipette is similar to Dittmar's, but with the special stop-cock and mercury bulb as in the absorption pipettes.

The phosphorus pipette consists of an ordinary Orsat's phosphorus pipette fitted with a horizontal stop-cock and fixed in a tin water vessel with aperture for thermometer.

The advantages of the apparatus as compared with that of Macfarlane and Caldwell's are—

An accurate correction tube, which really saves time and trouble.
A means of accurately adjusting the level of the mercury without taking one's eye from the reading telescope.
Greater cleanliness of the mercury in the measuring tube towards the end of an analysis.
The possibility of washing out the measuring tube, in case of accident, at any stage whilst the gas is in one of the pipettes.
Direct transference from pipette to pipette when desired.
The measuring tube constant in position.
A good illumination for reading always obtainable without trouble.
Explosion in a separate pipette.

Advantages, as compared with the Dittmar or similar apparatus—

Transference direct from measuring tube to pipette, instead of to and from an intermediate tube.
Easier manipulation and greater cleanliness, especially as regards the fatal introduction of absorbent into the measuring tube.
Pipettes giving more surface and better agitation.
A considerable reduction in the amount of mercury required.

SIMPLER METHODS OF GAS ANALYSIS.

All the sets of apparatus previously described are adapted to secure the greatest amount of accuracy, regardless of speed or of the time occupied in carrying out the various intricate processes involved.

For industrial and technical purposes the demand for something

requiring less time and care, even at the sacrifice of some accuracy, has been met by a large number of designs for apparatus of a simpler class, among which may be mentioned those of Orsat, Bunte, Winkel, Hempel, Stead, Lunge, etc. Many of these are arranged to suit the convenience of special industries, and will not be described here.

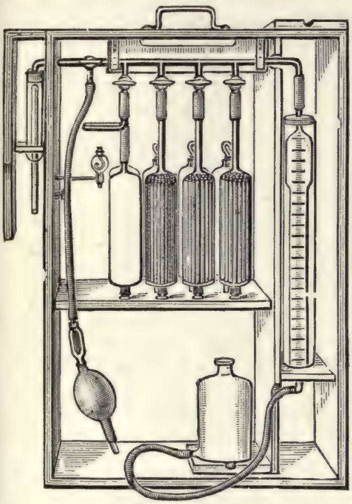


Fig. 106.

The most useful apparatus for general purposes is either that of Hempel or Lunge, both of which will be shortly described. Fuller details as to these and other special kinds of apparatus are contained in Winkler's *Handbook of Technical Gas Analysis*, translated by Lunge.*

The general principles upon which these various sets of apparatus are based, and the calculation of results, are the same as have been described in preceding pages; and of course due regard must be had to tolerable equality of temperature and pressure, and the effects of cold or warm draughts of air upon the apparatus whilst the manipulations are carried on. If the operator is not already familiar with methods of gas analysis, a study of the foregoing sections will be of great assistance in manipulating the apparatus now to be described.

Orsat-Lunge Gas Apparatus.—Fig 106. shows the outline of this instrument. The modification of the original Orsat instrument, by Lunge, is a contrivance for burning hydrogen and other gases by heated palladium asbestos. It is so well known and so constantly in use that no detailed description is needed here, but another form of the apparatus, which is intended for the determination of unburnt products in chimney gases, has been devised by W. H. Sodeau.† It is shown in fig. 107, and the description is as follows :—

In experimental work on the economic application of fuel, it is very desirable to know, whilst a trial is actually proceeding, not only what excess of air is being employed, but also the amount of unburnt gases.‡ Combining these data with the indications of a thermojunction placed at the base of the funnel, one can follow throughout the trial the total amount of heat (potential as well as actual) which is passing up the chimney. With a given boiler, for example, if one takes care of the exit gases, the evaporation will practically take care of itself. The fuel employed represents a certain total amount of heat, and the loss by radiation

* Gurney and Jackson, 2nd edition, 1902. † *C. N.* **89**, 61.

‡ When working with very limited furnace space, as in naval water-tube boilers of the "Express" type, a reduction of the "excess" of air may cause large amounts of combustible gases to escape unburnt, and so lead to decreased, instead of increased, evaporative efficiency.

from the boiler will be practically uniform; hence the evaporation per pound of fuel may be gauged by what remains after deducting the various losses from the calorific value of the fuel, or, in other words, by working up the chimney gas results as in a "heat balance sheet."

This method of checking the evaporative efficiency is especially advantageous in short experimental runs, as feed water is not always read with much accuracy, and all that passes through the main stop valve may not actually be steam.

The actual analytical problem may be reduced to the rapid determination of carbon dioxide, carbon monoxide, and hydrogen (including hydrocarbons if present). It is, however, customary to determine the oxygen in chimney gases, whilst the determination of hydrogen is usually omitted. The desirability of determining the amount of hydrogen is illustrated by the table below, in which are given a few analyses of the products of incomplete combustion obtained in some experiments with a 1000 horse-power water-tube boiler of the "Express" type. With Welsh coal the loss as unburnt hydrogen usually amounted to nearly a third of the loss as carbon monoxide, whilst with petroleum the proportion averaged about two-thirds. This difference was no doubt mainly due to the larger proportion of total hydrogen present when oil-fuel was employed.

Examples of Incomplete Combustion.

	Welsh coal				Crude Texas oil (steam sprayed).			
Carbon dioxide, per cent. ..	9·0	11·0	9·9	9·2	6·1	9·5	9·0	7·9
Carbon monoxide, per cent.	2·15	2·8	1·65	1·3	2·1	1·5	1·0	0·6
Hydrogen, per cent. ..	0·65	0·55	0·47	0·4	1·2	1·0	0·6	0·4
Pounds air per pound fuel	17·2	14·7	17·75	19·5	25·7	19·45	21·35	25·0
Excess air per cent. above theoretical	55·0	32·3	60·0	75·7	84	39	53	79
Evaporation units* per pound of fuel lost as combustible gases ..	2·34	2·26	1·71	1·51	3·65	2·05	1·45	1·06

Air being practically constant in composition it is unnecessary to determine the oxygen in chimney gases if the approximate composition of the fuel is known, for it is then easy to work out simple formulæ by means of which those data which are of practical importance may be calculated with fair accuracy from the percentages of carbon dioxide, carbon monoxide, and hydrogen alone.

Take, for example, two analyses of fuels:—

	Welsh coal.	Texas petroleum.
Carbon	88·2	85·0
Sulphur	0·77	1·34
Hydrogen	2·6	12·0
Ash, oxygen, &c.	8·43	1·66
	100·0	100·0
Theoretical amount of air for 1 pound fuel	11·1 lb.	13·95 lb.

Using CO_2, CO, and H_2 respectively to denote the percentages of carbon dioxide, carbon monoxide, and hydrogen in the chimney gases, the following formulæ may be obtained by calculation from the equations for combustion:—

Welsh coal. Texas petroleum.

1. Pounds air per pound of fuel—

$$\frac{204 - CO}{CO_2 + CO} + 0{\cdot}28 \qquad \frac{206 - CO}{CO_2 + CO} + 0{\cdot}84$$

2. Excess air per cent. above theoretical—

$$\frac{1837 - 9\ CO}{CO_2 + CO} - 97{\cdot}5 \qquad \frac{1476 - 7{\cdot}4\ CO}{CO_2 + CO} - 94{\cdot}1$$

3. Evaporation units lost as unburnt gases—

Welsh coal, Texas petroleum.

$$9{\cdot}33 \frac{CO + H_2}{CO_2 + CO} \qquad 9{\cdot}04 \frac{CO + H_2}{CO_2 + CO}$$

* An "evaporation unit" is the amount of heat required to convert one pound of water at 100° C. into steam at the same temperature.

These formulæ will, of course, apply only to fuels having the composition given above. For ordinary purposes the terms including CO may be omitted from the numerators of formulæ (1) and (2). Curves can then be plotted having $CO_2 + CO$ on one axis, and either "pounds air per lb. of fuel" or "excess air per cent. above theoretical" on the other, so that the meaning of an analysis can be seen at a glance.

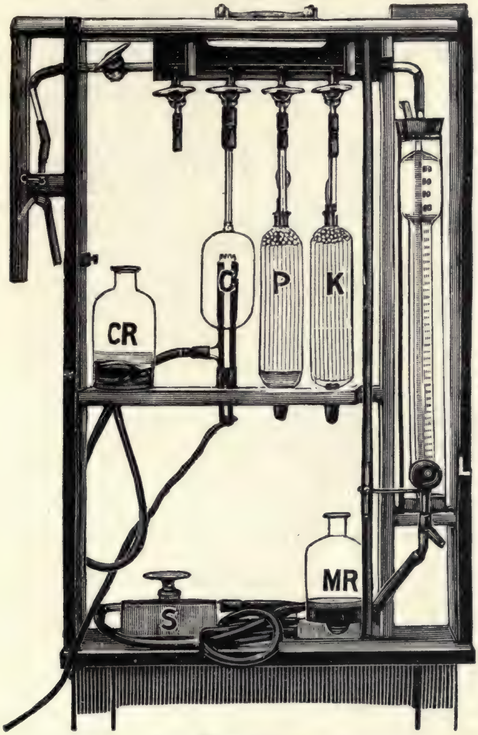


Fig. 107.

An ordinary Orsat apparatus affords a ready means of determining the carbon dioxide, but the absorption of carbon monoxide by means of that somewhat objectionable re-agent, cuprous chloride, involves the previous removal of oxygen by means of phosphorus or alkaline pyrogallol, absorbents which act exceedingly slowly when too cold. This method takes no account of free hydrogen (or saturated hydrocarbons). The author decided to discard absorption by cuprous chloride in favour of a combustion method, and not finding the capillary combustion tube of palladinized asbestos (as fitted in the Orsat-Lunge apparatus) quite suitable for use in the stokehold, finally adopted an Orsat apparatus modified as shown in the accompanying figure, in which the main feature is an adaptation of the Winkler combustion pipette.*

A large glass stop-cock, S, of 4 to 5 mm. clear bore, is attached to the base of the apparatus, one end being connected to the measuring tube and the other to the reservoir MR. The pipette, K, is of the ordinary form, and contains caustic potash solution (one part potash to two of water). A similar pipette, P, containing phosphorus or alkaline pyrogallol, may be used if it is desired to determine

* The Winkler pipette, a development of Coquillon's "Grisoumeter," is described and figured in Winkler and Lunge's "Technical Gas Analysis," pp. 151–155.

the oxygen. The combustion pipette, C, may be made from the commercial form of Winkler pipette by simply cutting off the U-tube and sealing on a straight piece of capillary tube of suitable length. An ordinary Hempel pipette for solid absorbents may be altered in a similar manner, the neck at the bottom being closed by a two-hole rubber stopper through which passes a pair of unlacquered brass electrodes bridged across by a platinum spiral made by coiling about 4 cm. of platinum wire of about 0·3 mm. diameter around a needle 1·3 mm. thick.

When the combustion pipette is employed with mixtures rich in combustible gases the coil must be near the top of the bulb in order that serious explosions may be avoided, but for the analysis of any ordinary chimney gases the coil may be placed much lower in order to reduce the heating of the glass. The gas may then be returned as soon as the current is cut off, without waiting for the glass to cool.

A fixed bulb* as in the Hempel (or Orsat) pipette, may be employed to receive the displaced water unless it is desired to carry out the rapd determination of carbon monoxide and hydrogen together, as described below, when the bulb, C, should be connected by means of india-rubber tubing to the reservoir, C R, consisting of a small aspirator bottle, similar to that connected to the measuring tube. When in use the spiral is raised to a white heat by means of a two-cell accumulator, the current being conveniently adjusted to the right strength by passing it through a few feet of the tinned iron wire, about $\frac{1}{64}''$ diameter, which is commonly sold in penny skeins.

In order to eliminate parallax the measuring tube is read by means of a lens mounted in conjunction with an eye-cap, and sliding on a brass rod, as employed in connection with the "Kew principle" correction tube.† Before each reading is taken, the water in the measuring tube is allowed to drain down for one minute, as indicated by the sand-glass used for timing the absorptions and combustions.

The U-tube filled with glass wool ordinarily supplied with the Orsat apparatus being somewhat apt to clog if dense black smoke is produced, it is conveniently replaced by a simple T piece having a small plug of glass wool in the limb through which the sample enters the apparatus. In this way only the actual samples are filtered, and the solid particles in the main stream pass direct to the aspirator.

METHOD OF PROCEDURE: The measuring off of the sample is effected in the usual manner, except that it is convenient to close S instead of pinching the india-rubber tube when adjusting the water to the zero mark prior to bringing the gas to atmospheric pressure.

Carbon dioxide is determined by sending the greater part of the gas over into K and back again, then leaving it for one minute to complete the absorption, and measuring again as usual; the decrease gives the percentage of carbon dioxide. The current is next switched on, and the gas passed over into the combustion pipette, C, where it remains for one minute, being then returned to the measuring tube (after switching off the current), and the contraction noted.

The carbon dioxide produced is then determined by a one-minute absorption in the potash pipette, K; the decrease gives the percentage of carbon monoxide.

As carbon monoxide unites with half its volume of oxygen to form its own volume of carbon dioxide, it follows that half the amount of the carbon monoxide found must be deducted from the contraction during combustion. Two-thirds of the corrected contraction equals the percentage of hydrogen.

For example, if the contraction on combustion amounted to 2·3 c.c. and the resulting carbon dioxide to 1·6 c.c., then the gas contained 1·6 per cent. of carbon monoxide and $\frac{2}{3}\left(2{\cdot}3-\frac{1{\cdot}6}{2}\right)=\frac{2}{3}\times 1{\cdot}5=1{\cdot}0$ per cent. of hydrogen. It should be noted that the only absorbent employed is one which is readily obtained and seldom needs renewing. The determination of carbon dioxide, carbon monoxide, and hydrogen by the above method can be completed in fifteen minutes. Any traces of hydrocarbons, if present, will of course appear partly as carbon monoxide

* The ordinary Hempel pipette is sometimes supplied with a bulb too small to contain the water displaced by the heated gas.

† J. S. C. I., 1903, 22, 188, 189.

and partly as hydrogen in the above method of analysis. Their heat value will not be fully represented, but this is an unimportant defect, and it exists more markedly in the old cuprous chloride method.

It may occasionally be desirable to know the percentage of oxygen originally present in the gas. This may be found by finally absorbing with phosphorus or pyro in the pipette P, and adding to the result the amount of oxygen required to burn the combustible gases.

RAPID JOINT DETERMINATION OF CARBON MONOXIDE AND HYDROGEN.—This may be carried out by omitting the measurement immediately after combustion, and transferring the gas direct from C to K in the following manner:—After the carbon dioxide has been determined, open the stop-cock attached to C, and switch on the current, raising the reservoir, M R, so as to drive the gas into C. Close S when the water has risen to the top of the measuring tube, and about one minute later switch off the current and open the stop-cock of K, raising the reservoir, C R, so as to drive the gas over into the potash, and finally closing the stop-cock of C. After allowing one minute for absorption, the stop-cock, S, is opened, the residue drawn back into the measuring tube, and the stop-cock of K then closed. Two-thirds of the contraction so produced equals the percentage of "combustible gases," *i.e.*, carbon monoxide and hydrogen, in the sample.

The result so obtained is translated into "evaporation units" by means of a formula similar to 3, the denominator being replaced by $CO_2 + (\frac{3}{4} \times \text{combustible gases})$ in the case of Welsh coal, and by $CO_2 + (\frac{2}{3} \times \text{combustible gases})$ when Texas oil is employed. The amount of air is similarly found by means of formulæ or curves.

When collecting samples of chimney gas for subsequent analysis the sometimes troublesome process of saturating water during the trial may be avoided by appropriately diluting a saturated solution of carbon dioxide. Thus, if the gas is expected to contain about 12 per cent. of carbon dioxide, the sample bottles should be filled with a mixture of seven parts tap-water and one part of water saturated with carbon dioxide. The flow of water from the sample bottle may be conveniently regulated by attaching, say, a yard of tubing (in order to give a fairly uniform head), to the end of which is connected a "wash-bottle jet" which has previously been found to permit the emptying to take place in the required time. The jet is less likely to clog if used in the reversed position.

Simple Titration of Gases.—Many instances occur in which the amount of a given constituent in a gaseous mixture can be determined by aspirating the sample through a solution which effects selective absorption of the constituent to be determined. Analysis of the solution enables the weight and volume of the absorbed gas to be calculated; the volume of the residual gases with which it was associated is obtained by measuring the volume of water discharged by the aspirator employed or by passing the gases through a gas meter. Two methods of testing are in general use:—

1. The Continuous Method, whereby a portion of the gas is aspirated slowly and continuously over a long period through absorbing vessels by means of a water jet pump or water aspirator of large size.
2. The Intermittent Method, whereby separate tests are taken at intervals throughout the day or from day to day.

The former method is in use in the larger chemical works where an exact measure of loss is desired by day and night; the latter is in general use in all works where testing is done, and is employed by the Inspectors appointed under The Alkali, etc. Works Regulation Act, 1906, for their routine testing to control the escape

of acid and other gases scheduled as " noxious and offensive gases " by the Act.

In the Intermittent Method the standard solutions employed are generally so arranged as to minimise calculations, the volume of standard solution used for titration giving directly the weight of constituent in grains per cubic foot of escaping gases. The absorbing vessels used in the works are generally of glass with an aspirator attached of unknown capacity. The Alkali Inspectors prefer a collapsible rubber aspirator, such as the Fletcher's bellows aspirator, as being more portable and less liable to breakage. The absorbing liquid in this case is placed inside the aspirator ; gas and liquid are brought into contact by vigorous shaking, and the latter subsequently expelled for titration. The capacity of the bellows on expansion being known, the weight and volume of the condensed products can be readily calculated.

In testing chlorine-exits a rubber enema-pump is often employed to draw the gases through the absorbing solution, which is of such strength that a certain number of deliveries of the bulb indicate a definite quantity of chlorine when the colour of the liquid changes.

Detailed descriptions of the various methods of determining the amount of acid and other noxious constituents of gaseous mixtures by selective absorption will be found in Lunge's " Sulphuric Acid and Alkali" and in Lunge's "Technical Chemists' Handbook." The reader should also consult the Alkali Reports, especially that for 1902.

Normal Solutions for Gas Analysis.—In the titration of gases by these methods, particularly on the Continent, the custom is to use special normal solutions, 1 c.c. of which represents 1 c.c. of the absorbable gas in a dry condition and at 760 mm. pressure and 0°C temperature. These solutions must not be confounded with the usual normal solutions used in volumetric analysis of liquids or solids. For instance, a normal gas solution for chlorine would be made by dissolving 4·4917 gm. of As_2O_3, with a few grams of sodium carbonate to the litre, and a corresponding solution of iodine containing 11·522 gm. per litre, in order that 1 c.c. of either should correspond to 1 c.c. of chlorine gas. 1 c.c. of the same iodine solution would also represent 1 c.c. of dry SO_2, and so on.

A very convenient bottle for the titration of certain gases is adopted by Hesse. It is made in a conical form, like an Erlenmeyer's flask, and has a mark in the short neck, down to which is exactly fitted a caoutchouc stopper having two holes, which will either admit the jet of a burette or pipette, or may be securely closed by solid glass rods. The exact content of the vessel up to the stopper is ascertained, a convenient size being about 500 or 600 c.c. The exact volume is marked upon the vessel.

In the case of gases not affected by water, the bottle is filled with that liquid and a portion displaced by the gas, and the stopper with

its closed holes inserted. If water cannot be used, the gas is drawn into the empty bottle by means of tubes with an elastic pump. The absorbable constituent of the gas is then determined with an excess of the standard solution run in from a pipette or burette. During this operation a volume of the gas escapes equal to the volume of standard solution added, which must of course be deducted from the contents of the absorbing vessel. The gas and liquid are left to react with gentle shaking until complete. The excess of standard solution is then found residually by another corresponding standard solution ; and in the case of using gas normal solutions, the difference found corresponds to the volume of the absorbed constituent of the gas in c.c. ; and from this, and from the total volume of gas employed, may be calculated the percentage, allowing for the correction mentioned. This arrangement may be used for CO_2 in air, using normal gas barium hydrate and a corresponding normal gas oxalic acid with phenolphthalein. The normal oxalic acid should contain 5·6314 gm. per litre, in order that 1 c.c. may represent 1 c.c. of CO_2. The baryta solution must correspond, or its relation thereto found by blank experiment at the time. The arrangement is also available for HCl in gases, using a normal gas silver solution containing 4·8488 gm. Ag per litre, as absorbent, with a corresponding solution of thiocyanate (p. 145) and ferric indicator ; or the HCl may be absorbed by potash, then acidified with HNO_3, and the titration carried out by the same process ; or again, an alkali carbonate may be used, and the titration made with a normal gas silver solution using the chromate indicator (p. 142).

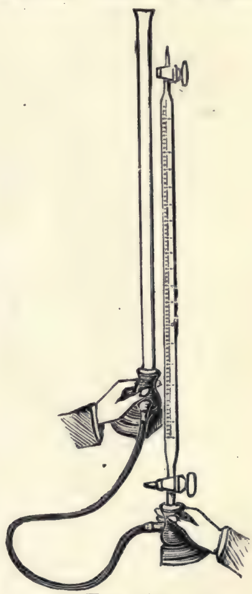


Fig. 108.

Hempel's Gas Burette.—This consists of two tubes of glass on feet, one of which is graduated to 100 c.c. in $\frac{1}{5}$ c.c. (the burette proper), and the other plain (the pressure tube). They are connected at the feet by an elastic tube, much in the same way as Lunge's nitrometer. The arrangement is shown in fig. 108.

The illustration shows the burette with three-way stop-cock at bottom, which is necessary in the case of gases soluble in water, or where any of the constituents are affected thereby. If this is not the case, a burette without such stop-cock is substituted (fig. 109). The elastic tube should not be in one piece, but connected in the middle by a short length of glass tube to admit of ready disconnection.

Fig. 109 illustrates not only the original Hempel burette with pressure tube, but also the method of connection with the gas

pipette, and the way in which the elastic tube is joined by the intervening glass tube.*

Hempel, with great ingenuity, has devised special pipettes to be used in connection with the burette, which render the instrument very serviceable for general gas analysis. The pipette

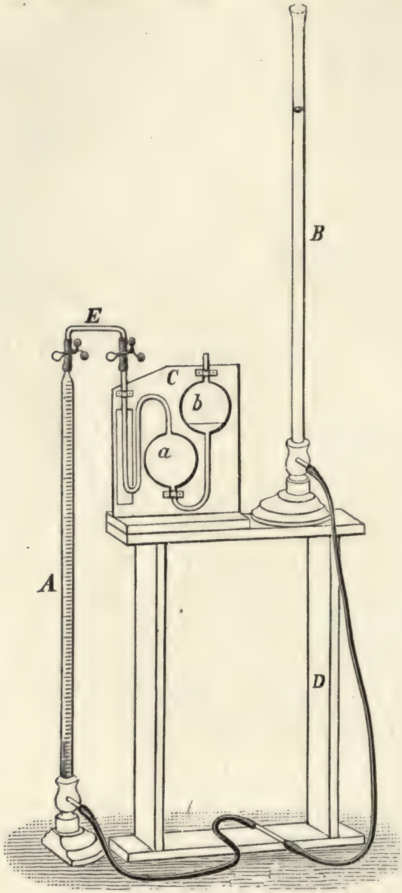


Fig. 109.

shown in fig. 109 is known as the simple absorption pipette, and serves for submitting the gas originally in the burette to the action of some special absorbent. With a series of these pipettes the gas is submitted to the action of special absorbents, one after another,

* The same chemist has since designed a gas burette which has the advantage of being unaffected by the fluctuating temperature and pressure of the atmosphere. This is effected by connecting the measuring apparatus with a space free from air, but saturated with aqueous vapour. A figure showing the arrangement is given in *C. N.* **56**, 254. These simpler forms of gas apparatus in great variety, including various forms of the nitrometer, are kept in stock by most of the dealers in apparatus in the kingdom.

until the entire composition is ascertained. The connections must in all cases be made of best stout rubber, and bound with wire.

Collection and measurement of the Gas over Water.—Both tubes are filled completely with water (preferably already saturated mechanically with the gas), care being taken that all air is driven out of the elastic tube. The clip is then closed at the top of the burette, and the bulk of the water poured out of the pressure tube, the elastic tube being pinched meanwhile with the finger and thumb to prevent air entering the burette. The latter is then connected by a small glass tube with the source of the gas to be examined, when, by lowering the pressure tube, the gas flows in and displaces the water from the burette into the pressure tube. The pressure is then regulated by raising or lowering either of the tubes until the water is at the same level in both, when the volume of gas is read off. It is convenient of course to take exactly 100 c.c. of gas to save calculation.

Collection and measurement of the Gas without Water.—In this case the three-way tap burette (fig. 108) is dried thoroughly by first washing with alcohol, then ether, and drawing air through it. The three-way tap is then closed, the upper tube connected with the gas supply, and the burette filled either by the pressure of the gas, or by using a small pump attached to the three-way cock to draw out the air and fill the burette with the gas. When full the taps are turned off, and connection made with the pressure tube, which is then filled with water, the tap opened so that the water may flow into the burette and absorb the soluble gases present. As the burette holds exactly 100 c.c. between the three-way tap and the upper clip, the percentage of soluble gas is shown directly on the graduation.

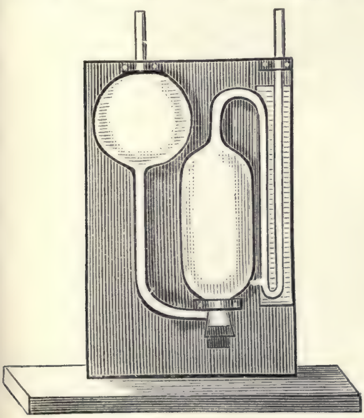


Fig. 110.

The method of Absorption.—In the case of the simple pipette fig. 109, *a* is filled with the absorbing liquid, which reaches into the siphon bend of the capillary tube ; the bulb *b* remains nearly empty. In order to fill the instrument, the liquid is poured into *b*, and the air sucked out of *a* by the capillary tube. It is convenient to keep a number of these pipettes filled with various absorbents, well corked, and labelled.

Another pipette of similar character is shown in fig. 110, and is adapted for solid reagents, such as stick phosphorus in water. The instrument has an opening at the bottom, which can be closed with a caoutchouc stopper. This pipette is also used for absorbing CO_2 by filling it with plugs of wire gauze and caustic potash solution, so as to expose a large active surface when the liquid is displaced by the gas.

To make an absorption, the capillary U-tube is connected with the burette containing the measured gas by a small capillary tube (fig. 110), the pinch-cock of course being open, then by raising the pressure tube, the gas is driven over into the cylindrical bulb, where it displaces a portion of the liquid into the globular bulb. When the whole of the gas is transferred, the pinch-cock is closed, and the absorption promoted by shaking the gas with the reagent. When the action is ended, communication with the burette is restored, and the gas siphoned back by means of the pressure tube into the burette to be measured.

The double absorption Pipette, shown in fig. 111, is of great utility in preserving absorbents which would be acted on by the air, such for instance as alkaline pyrogallol, cuprous chloride, etc. The bulb next the siphon tube is filled with the absorbent, the next is empty, the third contains water, and the fourth is empty. When the gas is passed in, the intermediate water passes on to the last bulb to make room for the gas, thus shutting off all contact with the atmosphere, except the small amount in the second bulb. An arrangement is also made for the use of solid reagents, by substituting for the globe next the U capillary tube a cylindrical bulb as in fig. 110.

Hydrogen Pipette.—The hydrogen gas necessary for explosions or combustions is produced from a hollow rod of zinc fixed over a glass rod passed through the rubber stopper (fig. 110). The bulb being filled with dilute acid, gas is generated, and as it accumulates the acid is driven into the next bulb and the action ceases.

Explosion Pipette.—Another arrangement provides for explosions by the introduction into a thicker bulb of measured volumes of the gas, of air, and of hydrogen. The bulb being shut off with a stop-cock, a spark is passed through wires sealed into the upper portion of the bulb.

Pipette with Capillary Combustion Tube.—This simple arrangement consists of a short glass capillary tube bent at each end in a right-angle, into which an asbestos fibre impregnated with finely divided palladium is placed, so as to allow of the passage of the gas.*

* To prepare palladium asbestos, dissolve about 1 gm. palladium in *aqua regia*, evaporate to dryness on water-bath to expel all acid. Dissolve in a very small quantity of water, and add 5 or 6 c.c. of saturated solution of sodium formate, then sodium carbonate until strongly alkaline. Introduce into the liquid about 1 gm. soft, long-fibred asbestos, which should absorb the whole liquid. The fibre is then dried at a gentle heat, and finally in the water-bath till perfectly dry; it is then soaked in a little warm water, put into a glass funnel, and all adhering salts washed out carefully without disturbing the palladium deposit. The asbestos so prepared contains about 50 per cent. Pd, and in a perfectly dry state is capable of causing the combination of H and O at ordinary temperature, but when used in the capillary tube it is preferable to use heat as mentioned. The capillary combustion tubes are about 1 mm. bore and 5 mm. outside diameter, with a length of about 15 cm. The fibre is placed into them before bending the angles, as follows :—Lay a few loose fibres, about 4 cm. long, side by side on smooth filter paper, moisten with a drop or two of water, then by sliding the finger over them twist into a kind of thread about the thickness of darning cotton. The thread is taken carefully up with pincers and dropped into the tube held vertically, then by aid of water and gentle shaking moved into position in the middle of the tube. The tube is then dried in a warm place, and finally the ends bent at right-angle for a length of 3½ to 4 cm. Platinum asbestos may be prepared in the same way, using, however, only from half to one-fourth the quantity of metal.

The gas being mixed with a definite volume of air in the burette, and the measure ascertained (not more than 25 c.c. of gas and 60 or 70 c.c. of air), the asbestos tube is heated gently with a small gas flame or spirit lamp, and the pinch-cocks being opened, the mixture is slowly passed through the asbestos and back again, the operation being repeated so long as any combustible gas remains. No explosion need be feared. The residue of gas ultimately obtained is then measured, and the contraction found; from this the volume of gas burned is ascertained either directly, or by the previous removal of CO_2 formed by the combustion with the potash pipette. H is very easily burned, CO less easily. Ethylene, benzene, and acetylene require a greater heat and longer time. CH_4 is not affected by the method, even though mixed with a large excess of combustible gases.

In order to illustrate the working of the whole set of apparatus, the analysis of a mixture containing most or all of the gases likely to be met with in actual testing is given from a paper contributed by Dr. W. Bott.* The mixture of gases consists of CO_2, O, CO, C_2H_4, CH_4, H and N. A sample of this gas—say 100 c.c.—is collected and measured in the gas burette. The CO_2 is next absorbed by passing the gas into a pipette (fig. 109) containing a solution of 1 part of KHO in 2 parts of water. To ensure a more rapid absorption, the bulb shown in fig. 110 containing the caustic potash may be partly filled with plugs of wire gauze. The absorption of the CO_2 is almost instantaneous. It is only necessary to pass the gas into the apparatus and siphon it back again to be measured. The contraction produced gives directly the percentage of CO_2 since 100 c.c. were used at starting.

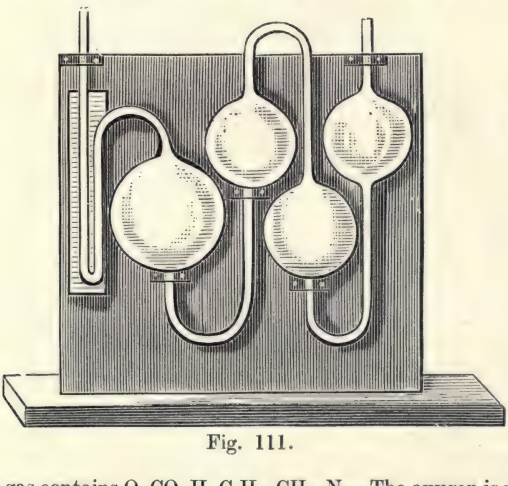


Fig. 111.

The remaining gas contains O, CO, H, C_2H_4, CH_4, N. The oxygen is next absorbed. This may be effected in two ways—by means of moist phosphorus or by an alkaline solution of pyrogallic acid. The former method is by far the more elegant of the two, but not universally applicable. The absorption is done in a pipette (fig. 110), the corked bulb of which is filled with thin sticks of yellow phosphorus surrounded by water. The gas to be tested is introduced in the usual manner, and by displacing the water comes into contact with the moist surface of the phosphorus, which speedily absorbs all the oxygen from it. The absorption

* *J. S. C. I.* 4, 160.

proceeds best at about 15-20° C., and is complete in ten minutes. The small quantity of P_2O_3 formed by the absorption dissolves in the water present, and thus the surface of the phosphorus always remains bright and active. This neat and accurate method is not however universally applicable ; the following are the conditions under which it can be used :—The oxygen in the gas must not be more than 50 per cent., and the gas must be free from ammonia, C_2H_4 and other hydrocarbons, vapour of alcohol, ether and essential oils. In the instance chosen, the phosphorus method would hence not be applicable, as the mixture contains C_2H_4 ; therefore pyrogallol must be used. The absorption is carried out in the compound absorption pipette (fig. 111), the bulb of which is completely filled with an alkaline solution of pyrogallol made by dissolving 1 part (by volume) of a 25 per cent. pyrogallol solution in 6 parts of a 60 per cent. solution of caustic potash. The absorption is complete in about five minutes, but may be hastened by shaking. The remainder of the gas now contains C_2H_4, CO, CH_4, H, N, and the next step is to absorb the C_2H_4 by means of fuming SO_3, the CH_4 being subsequently determined by explosion. In choosing the latter method a portion, say half, of the residual gas is taken for the determination of hydrogen. The absorption of the hydrogen is based on the fact that palladium black is capable of completely oxidizing hydrogen when mixed with excess of air, and slowly passed over the metal at the ordinary temperature. About $1\frac{1}{2}$ gm. of palladium black are placed in a small U-tube plunged into a small beaker of cold water, and the gas, mixed with an excess of air (which, of course, must be accurately measured), is passed slowly through the tube two or three times,* the tube at the time being connected with an ordinary absorption pipette filled with water or else with the KOH pipette, which in this case, of course, simply serves as a kind of receiver. Finally the gas is siphoned back into the burette and measured—two-thirds of the contraction correspond to the amount of H originally present in the mixture of gas and air. The CH_4 is not attacked by ordinary 30 per cent. SO_3 Nordhausen acid during the absorption of the C_2H_4. The acid is contained in an absorption pipette (fig. 110), the bulb of which is filled with pieces of broken glass so as to offer a larger absorbing surface to the gas. The absorption is complete in a few minutes, but the remaining gas previous to measuring should be passed into the KOH pipette and back again, so as to free it from fumes of SO_3. Residual gas : CO, CH_4, H, N. The CO is next absorbed by means of an ammoniacal solution of cuprous chloride in a compound absorption pipette. The gas has to be shaken with the absorbent for about three minutes. It must be borne in mind that Cu_2Cl_2 solution also absorbs oxygen, and, according to Hempel, considerable quantities of C_2H_4, hence these gases must be removed previously. Residue : CH_4, H, N. Both CH_4 and H may now be determined either by exploding with an excess of air in the explosion pipette and measuring (1) the contraction produced, and (2) the amount of CO_2 formed (by means of the KOH pipette) ; or, according to Hempel, absorb the hydrogen first of all as described above—provided the U-tube be kept well cooled with water, inasmuch as that at about 200° C. a mixture of air and CH_4 is also acted upon by palladium. The presence of CO, vapours of alcohol, benzene and hydrochloric acid also interfere with the absorption by palladium.

The palladium may be used for many consecutive experiments, but must be kept as dry as possible. After it has been used for several absorptions it may be regenerated by plunging the tube into hot water and passing a current of dry air through it.

Having determined the hydrogen, the CH_4 in the remaining portion of the gas has to be determined. This contains CH_4, N and H, the amount of the latter being known from the previous experiment. The gas is mixed with the requisite quantity of air and hydrogen, introduced into the explosion pipette and fired by means of a spark. The water resulting from the combustion condenses in the bulb of the pipette, whilst the CO_2 formed is absorbed by the KOH solution present. Hence the total contraction produced corresponds to :

a. The hydrogen present in the original gas $+\frac{1}{2}$ its vol. of O (the quantity requisite for complete combustion).

b. The known quantity of hydrogen added $+\frac{1}{2}$ its vol. of O.

* Instead of this the H may be oxidized in the tube containing the palladium asbestos fibre previously described.

c. The CH_4 present +2 vols. of O requisite for its combustion.

$$\underbrace{\underbrace{CH_4}_{2} + \underbrace{O_4}_{4}} = \underbrace{(CO_2 + 2H_2O)}_{\text{disappears.}}$$

Since a and b are known, or can be readily calculated from the previous data, by subtracting $(a+b)$ from the total contraction it is possible to obtain $C-(a+b)=c$ contraction due to CH_4 alone, and one-third of this is equal to the volume of CH_4 present, as will readily be seen from the above equation.

The remaining nitrogen is obtained by difference.

Improved arrangement of Hempel's Pipettes for storing and using absorbents.—P. P. Bedson has designed an arrangement of pipettes which he uses in connection with a Dittmar's measuring apparatus, but which may of course be used with other forms of gas apparatus, by suitable connections. The pipettes are shown in fig. 112, and their use may be described as follows :—A capillary tube with a three-way cock A is fused to the Hempel pipette—the capillary is drawn out and bent so as to pass into the mercury trough. The tap A can be placed in connection with C, to which is attached a movable mercury reservoir D. In working, *e.g.*, transferring gas to E, the absorbent fills E and the capillary of tap A. By raising D the vessel C and capillary B are entirely filled with mercury. B, of course, is immersed in the mercury trough. Having filled B with mercury, the test tube containing the gas to be examined is brought over the end of B and some gas drawn into C by depressing D. The tap is then turned to put the tube in connection with E, and the gas forced into E by depressing the tube in trough. By raising and lowering the tube the gas can be brought into intimate contact with the absorbent and absorption thus promoted. To bring all the gas into E, D is again used and the remainder of gas drawn into C by depressing D; then by turning the tap round the gas from C can be forced into E; the tap is then turned so as to put the capillary and E in connection, and the gas flows into E with a small portion in capillary B, retained by the column of mercury filling the bent limb.

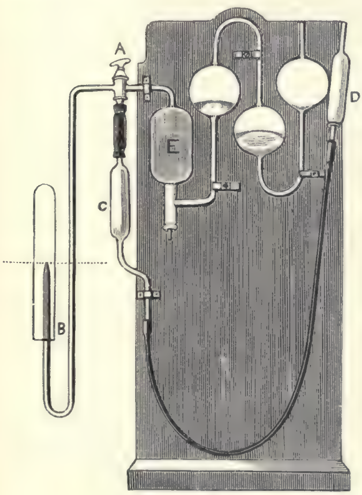


Fig. 112.

The gas may be left thus for some hours; and to transfer it to the tube, C and E are placed in connection by suitably turning the tap; then by depressing D some gas is drawn into C and the tap turned so as to put C and the tube in connection.

By carefully raising D the

mercury is washed out of B and some of the gas passes into the tube. With B clear of mercury and filled with gas, the tube and E are placed in connection and the gas flows out of E into the tube. When the liquid from E has risen so as to fill the vessel up to the tap (the capillary of the tap being also filled), the tap is turned to put C and B in connection ; then by raising D all gas is washed out of C and capillary into the tube used for its collection and transferred to the measuring tube.

Bedson also attaches to the measuring apparatus a vessel containing a known volume of air at known temperature and pressure, as recommended by Lunge, so as to dispense with the otherwise necessary corrections. Further details as to the various uses to which Hempel's gas pipettes and other simple forms of gas apparatus may be adapted, will be found in Hempel's *Gas Analysis* (Macmillan).

THE NITROMETER AND GAS-VOLUMETER.

(*For list of conversion factors, see p.* 285).

The nitrometer has been incidentally alluded to (page 286) as being useful for the determination of nitric acid in the form of nitric oxide. It was, indeed, for this purpose that the instrument was originally contrived, more especially for ascertaining the proportion of nitrogen acids in vitriol by Crum's process.

The instrument has also been found extremely useful for general technical gas analysis, and for the rapid testing of such substances as manganese peroxide, hydrogen peroxide, bleaching powder, urea, etc. The apparatus in its simplest form is shown in fig. 113, and consists of a graduated measuring tube fitted at the top with a three-way stopcock and a glass cup or funnel ; the graduation extends from the tap downwards to 50 c.c. usually, and is divided into $\frac{1}{10}$ c.c. The plain tube known as the pressure tube, is about the same size as the burette, and is connected with the latter by means of stout elastic tubing bound securely with wire. Both tubes are held in clamps on a stand, and

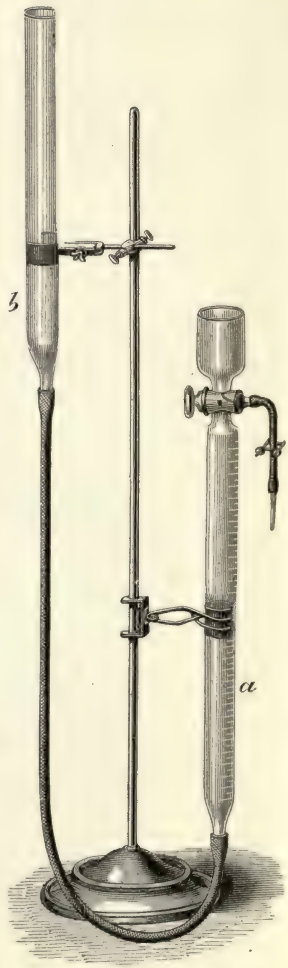


Fig. 113.

it is advisable to fix the burette itself into a strong spring clamp, so that it may be removed and replaced quickly.

One great advantage over many other kinds of technical gas apparatus which pertains to this instrument is that it is adapted for the use of mercury, thus ensuring more accurate measurements, and enabling gases soluble in water, etc., to be examined.

Another form of the same instrument is designed by Lunge for the determination of the nitric acid in saltpetre and nitrate of soda, where a larger volume of nitric oxide is dealt with than in many other cases. In this instrument a bulb is blown on the burette just below the tap, and the volume contents of this bulb being found, the graduation showing its contents begins on the tube at the point where the bulb ends, and thence to the bottom; the pressure tube also has a bulb at bottom to contain the mercury displaced from the burette. Illustrations of this form of nitrometer will be found further on.

The following description of the manipulation required for *the determination of nitrogen acids in vitriol* applies to the ordinary nitrometer, and applies equally to the determination of nitrates in water residues and the like (see page 286) :—

The burette *a* is filled with mercury in such quantity that, on raising *b* and keeping the tap open to the burette, the mercury stands quite in the tap-hole and about two inches up the tube *b*. The tap is now closed completely, and from 0·5 to 5 c.c. of the nitrous vitriol (according to strength) poured into the cup. *b* is then lowered and the tap cautiously opened to the burette, and shut quickly when all the acid except a mere drop has run in, carefully avoiding the passage of any air. 3 c.c. of strong pure H_2SO_4 are then placed in the cup and drawn in as before, then a further 2 or 3 c.c. of the acid to rinse all traces of the sample out of the cup. *a* is then taken out of its clamp, and the evolution of gas started by inclining it several times almost to a horizontal position and suddenly righting it again, so that the mercury and acid are well mixed and shaken for a minute or two, until no further gas is evolved. The tubes are so placed that the mercury in *b* is as much higher than that in *a* as is required to balance the acid in *a*; this takes about one measure of mercury for 6·5 measures of acid. When the gas has assumed the temperature of the room, and all froth subsided, the volume is read off, and also the temperature and pressure from a thermometer and barometer near the place of operation. The level should be checked by opening the tap, when the mercury level ought not to change. If it rises, too much pressure has been given, and the reading must be increased a trifle. If it sinks, the reading must be slightly diminished. A good plan is to put a little acid into the cup before opening the tap; this will be drawn in if pressure is too low, or blown up if it is too high. These indications will serve as a guide for a more correct second determination.

To empty the apparatus ready for another trial, lower *a* and open the tap, then raise *b* so as to force both gas and acid into the cup; by opening the tap then outwards, the bulk of the acid can be collected in a beaker, the last drops being wiped out with blotting-paper. It is hardly necessary to say that the tap must be thoroughly tight, and kept so by the use of a little vaseline, taking care that none gets into the bore-hole.

The factors for nitrogen etc., are given on page 285.

It is evident that the nitrometer can be made to replace Hempel's burette if so required, by attaching to the side opening of the three-way tap the various pipettes previously described, or smaller

pipettes of the same kind to be used with mercury, as described by Lunge.*

The instrument will also be found useful for collecting, measuring, and analyzing the gases dissolved in water or other liquids. An illustration of this method is given by Lunge and Schmidt† in the examination of a sample of water from the hot spring at Leuk in Switzerland.

The determination of the dissolved gases was made in the nitrometer, arranged as shown in figs. 114 and 115 :—

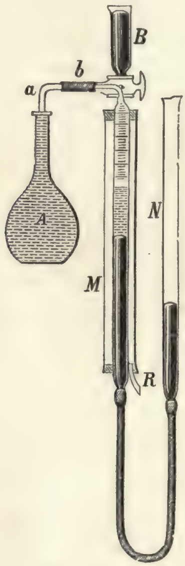


Fig. 114.

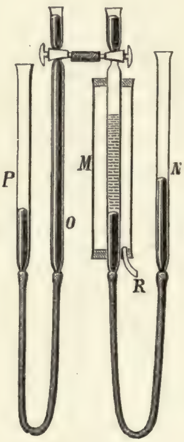


Fig. 115.

The flask A is completely filled with the water ; an india-rubber plug with a capillary tube (*a*) passing through it is then inserted in the flask, and the tube is thereby completely filled with water. The whole is then weighed, and the difference between this and the weight of the empty flask and tube gives the amount of water taken. The end of the capillary tube is then connected to the side tube of the nitrometer by the tube *b*. The nitrometer is then completely filled with mercury, and when the tubes are quiet, the flask and measuring tube of the nitrometer are quickly placed in connection, without the introduction of the slightest trace of air. The water in the flask is then slowly heated to boiling. Some water as well as the dissolved gases collect in the measuring tube of the nitrometer. The tube N of the nitrometer should be lowered in order that the boiling may take place under reduced pressure. After boiling for five to ten minutes, the stop-cock is quickly turned through 180°, so that the flask is placed in communication with the cup B containing mercury, and the flame removed.

Since the mercury stands lower in N than in M, it is not possible for any loss of gas to take place at the moment of turning the tap. It is also impossible for any gas or steam to escape through the mercury cup, since the pressure is inward. A small bubble of gas always remains under the stopper ; this is brought into M by lowering the tube N as much as possible, and then turning the stop-cock so

* *Berichte*, **14**, 14, 92. † *Z. a. C.* **25**, 309.

that the flask and measuring tube are again placed in connection, and when the bubble has passed over, quickly reversing the tap again.

When the whole of the gas is collected in the nitrometer, it is connected with a second instrument, O P, quite full of mercury. The gas is then transferred by placing the tap in such a position that it is closed in all directions, and the tube M is heated by passing steam through the tube R. When it is quite hot the tube N is lowered, causing the water in M to boil, thus expelling every trace of dissolved gas. The taps are then placed in connection and the gas passes over. It can then be cooled, measured, and submitted to analysis. Two experiments gave 505 gm. water taken, gas evolved 5·06 c.c., =10·02 per 1000 gm. 502 gm. water taken, gas evolved 4·94 c.c., =9·84 per 1000 gm.

Lunge's Improved Nitrometer for the Gas-Volumetric Analysis of Permanganate, Chloride of Lime, Manganese Peroxide, etc.—Lunge* in describing this instrument says :—

"In a paper published in the *Chemische Industrie*, 1885, 161, I described the manifold uses to which the nitrometer can be put as an apparatus for gas analysis proper, as an absorptiometer, and especially for gas-volumetric analyses. To fit it for the last-mentioned object, I added to it a flask, provided with an inner tube fused on to its bottom, and suspended from the side tube of the nitrometer, as shown in fig. 116, which at the same time exhibits the Greiner and Friedrich's patent tap. This shows how any ordinary nitrometer, such as are now found in most chemical laboratories, can be applied to the before-mentioned uses. Where, however, the methods concerned are to be employed not merely occasionally, but regularly, it will be preferable to get a nitrometer specially adapted to this use, of which figs. 117 and 118 show various forms. They have no cup at the top, which is quite unnecessary for this purpose, but merely a short outlet tube for air. Fig. 117 shows an instrument provided with one of the new patent taps, which are certainly very handy, and cause a much smaller number of spoiled tests than the ordinary three-way tap, as shown in fig. 118, which at the same time exhibits the form of nitrometer intended for large quantities of gas, the upper part being widened into a bulb, below which the graduation begins with either 60 or 100 c.c., ending at 100 or 140 c.c. respectively. There are also various shapes of flasks shown in these instruments, but it is unnecessary to say that these, as well as the bulb arrangements, can be applied to any other form of the instrument. The nitrometers used for gas-volumetric analyses are best graduated in such manner that the zero point is about a centimetre below the tap, whilst ordinary nitrometers have their zero point at the tap itself. I will say at once that for all determinations of oxygen in permanganate, bleach or manganese, it is quite unnecessary to employ mercury for filling the instruments, since identical results are obtained with ordinary tap water; but it is decidedly advisable to place this instrument, like any ordinary nitrometer or *any* other apparatus in which gases are to be measured, in a room where there are as few changes of temperature by cold draughts or gas-burners, and so forth, as possible.

"It may be as well to give here a general description of the mode of procedure for manipulating gas-volumetric analysis with the nitrometer, common to all analyses according to this method. Fill the nitrometer with water or mercury by raising the pressure tube till the level of the liquid in the graduated tube is at zero (in the case of instruments bearing the zero-mark a little below the tap, as in figs. 117 and 118), or at 1·0 c.c. (in the case of ordinary nitrometers beginning their graduation at the tap itself.) It is unnecessary to say that in the latter case all readings must be diminished by 1 c.c. Close the glass tap. Put the substance to be tested into the outer space of the flask, together with any other reagent apart from the H_2O_2 (in the case of bleaching-powder nothing but the bleach liquor, in that of permanganate the 30 c.c. of sulphuric acid, etc.). Now put the H_2O_2 into the inner tube of the flask, after having, in the case of testing for chlorine, made it alkaline in the previously described way. Put the india-

* *J. S. C. I.* **9**, 21.

rubber stopper still hanging from the tap, on to the flask, without warming the latter, as above described. As this produces a compression of the air within the flask, remove this by taking out the key of the tap in figs. 116, 117, or 118, turning it for a moment so as to communicate with the short outlet tube. Now turn the tap back, mix the liquids by inclining the flask, shake up and allow the action to proceed. As the gas passes over into the graduated tube, lower the pressure tube, so as to produce no undue pressure ; at last bring the liquid in both tubes to an exact level and read off.

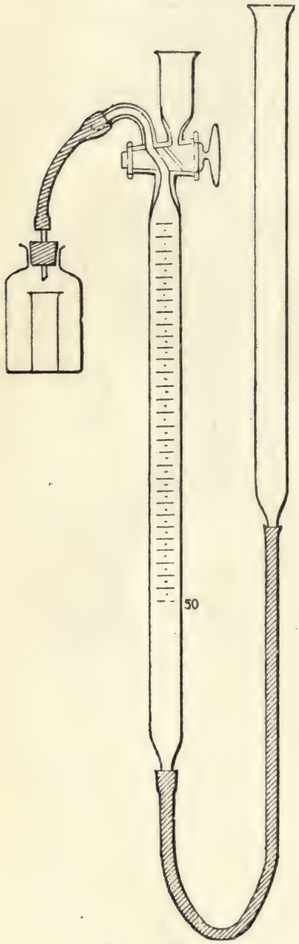


Fig. 116.

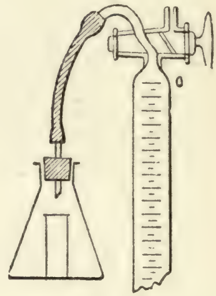


Fig. 117.

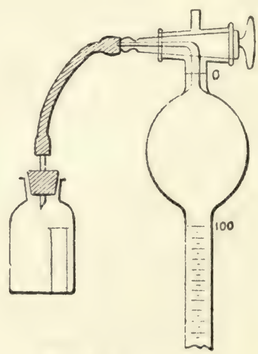


Fig. 118.

"In the case of bleach analysis all the oxygen of the chloride of lime is given off, together with exactly as much oxygen of the H_2O_2. The total is just equal to the volume of chlorine gas which would be given off by the chloride of lime, and thus immediately represents the French or Gay-Lussac chlorimetric degrees, of course after reducing the volume to 0° and 760 mm. pressure. (The reading of the barometer must be corrected by deducting the tension of aqueous

vapour for the temperature observed as well as the expansion of mercury, according to the tables found everywhere)."

Lunge's Gas-volumeter is an apparatus for dispensing with reduction calculations in measuring gas volumes (described by Lunge in *Zeitschrift f. angew, Chem.*, 1890, 139-144, and here quoted from *J. S. C. I.* ix. 547).

In technical gas analysis a considerable amount of time is taken up by calculations for reducing gas volumes to standard temperature and pressure. In pure gas analysis the inconvenience is not so great; for technical purposes the initial and end temperature and pressure may be taken as the same, owing to the short duration of the experiment, and for more accurate purpose "compensators" have been devised. Where, however, the gas to be measured is evolved from a weighed quantity of a liquid or solid (so that volume and weight have finally to be connected) the matter is different, and readings of thermometer and barometer have to be made, and then the necessary calculations have to be gone through. Tables of reduction have certainly been compiled for reduction of gaseous volumes at various temperatures and pressures to N.T.P., but readings of thermometer and barometer still have to be made, and only part of the time is saved. Further to reduce the time occupied and to render the technical chemist in this department to a great extent independent of temperature and atmospheric pressure the present apparatus has been constructed.

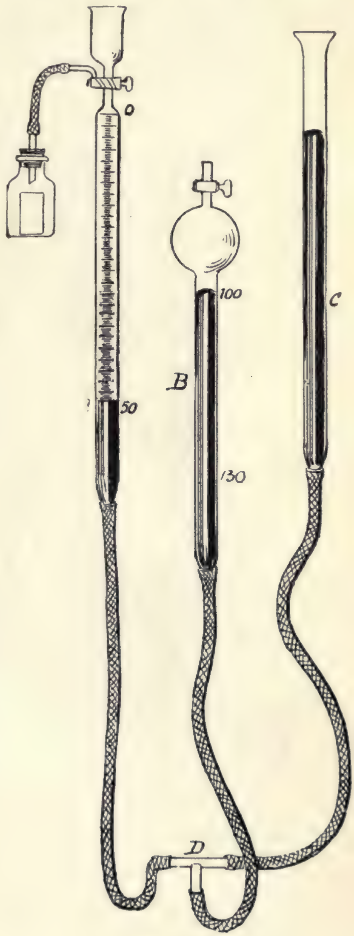


Fig. 119.

By means of a T-tube D (fig. 119), and thick-walled rubber tubing, are connected the three tubes A, B, C. A is for measuring the gas; it may be any form of nitrometer, a Bunte's burette or other convenient burette. B is the "reduction tube," which has at its upper end a spherical or cylindrical bulb. The volume to the first mark is 100 c.c., the remaining narrow portion of the tube being calibrated up to 130-140 c.c. in divisions representing $\frac{1}{10}$ c.c. This "reduction tube" is set once for all at the beginning of work by observing thermometer and barometer, calculating the volume which 100 c.c.

of perfectly dry air, measured at 0° C. and 760 mm. would occupy under the existing conditions. This quantity of air is then introduced, and the tube closed by means of the stop-cock shown, or by fusing up the inlet (having in place of the inlet tube shown in the figure a tube of capillary bore). If it be necessary to measure the gas moist a drop of water is introduced into this tube, and of course in the calculation necessary the barometric pressure must be reduced by the vapour tension of water; if the gases are to be measured perfectly dry (as, for instance, when using the nitrometer with sulphuric acid), a drop of sulphuric acid takes the place of the water.

C is the pressure tube.

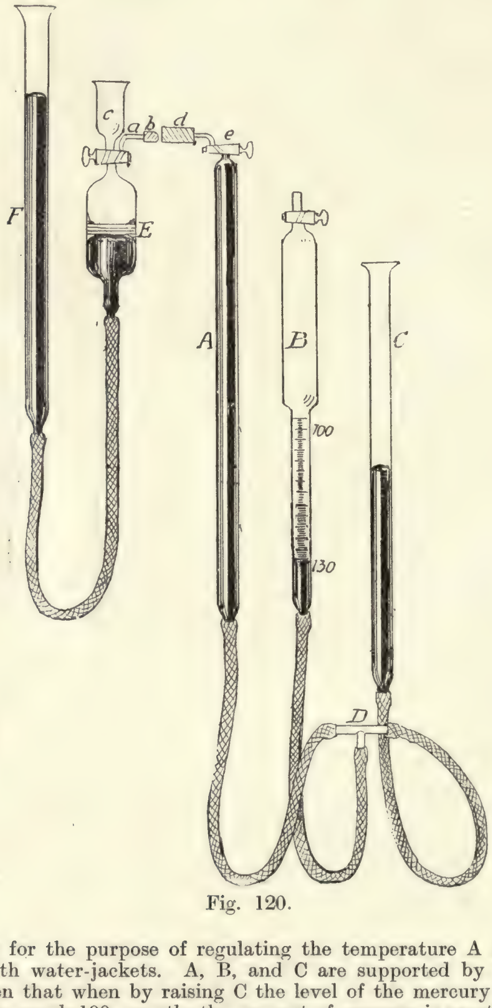


Fig. 120.

If necessary for the purpose of regulating the temperature A and B may be surrounded with water-jackets. A, B, and C are supported by spring clamps. It is easily seen that when by raising C the level of the mercury in B has been forced up to the mark 100, exactly the amount of pressure is exerted by C as will compress the gas in B to its volume under standard conditions.

In taking a reading A and B must be levelled and the mercury level in B must have been brought up to 100. The volume shown on A is then the volume reduced

to standard temperature and pressure. In cases where the gas is generated in A itself, or where the gas is transferred to A, this is all that need be done. If, however, the gas is generated in a side apparatus, as shown in fig. 119, A and C must first be levelled and the stop-cock of A then closed so that the gas in A is collected at atmospheric pressure. After this reduction may be effected as already explained.

In nitrogen determinations by Dumas' method, A contains caustic potash as well as mercury; this is compensated by having on the reduction tube, B, a mark at a distance below the 100 mark equal to one-tenth of the height of the caustic potash column (sp. gr. of the caustic potash equals one-tenth sp. gr. of mercury); when taking a reading the mercury in B must be at 100, and that in A must be on a level with this new lower mark of B. Similar allowance may be made in nitrometric determinations, but the case is here more difficult, owing to the variations in the quality and specific gravity of the sulphuric acid used. It is better in such cases to liberate the gas in a separate vessel and transfer subsequently to the burette for reduction and measurement. Fig. 120 shows a convenient form of apparatus. Of course the working part E, F need not be graduated. Before beginning the operation the mercury is made to fill E with the side tube *a*, which side tube is then capped with a caoutchouc stopper to prevent escape of the mercury during subsequent shaking. A, with its side tube, *e*, is also completely filled with mercury. The substance under examination, and subsequently the acid, are added through C as usual. To transfer the gas from E to A, the cap *b* is removed and *e* is fitted to *a* by means of the rubber connection *d*. F is then raised and C lowered, the taps are carefully opened, and transference effected until the acid in E just fills *e*.

A further saving of time may be effected in works, where the instrument is to be used always for one and the same object, by marking on the gas burette or nitrometer the weight in milligrams corresponding to certain volumes; this may be done either instead of or alongside the c.c. divisions; or, by using a fixed quantity of substance, percentages may be marked off directly. For nitrogen determinations by Dumas' method 1 c.c. of nitrogen under normal conditions weighs 1·2507 mgm. In the case of azotometric determinations of ammoniacal nitrogen (by sodium hypobromite) the graduations may be made to represent ammonia. Correction must be made in graduating, however, for the incompleteness of the reaction. Tables giving the corrections have been introduced, but the author has shown that these may be dispensed with, and that it is sufficient to make a correction of 2·5 per cent. For urea, however, the correction is 9 per cent.

The following table shows substances for which gasometric methods are used :—

Substances.	Basis to which Percentages are Calculated.	Method Employed.	Gas Evolved.	1 c.c. of Gas. = mgm. of Basis, (Col. II.)
Organic substances	Nitrogen	Dumas'	N	1·2507
Ammonia salts ..	,,	Hypobrmte.	N	1·285*
,, ,,	Ammonia	,,	N	1·561*
Urine	Urea	,,	N	2·952*
Bone-charcoal, etc.	Carbon dioxide	Decomposed with HCl	CO_2	1·966
,, ,,	Calcium carbonate	,,	CO_2	4·468
Pyrolusite	Manganese dioxide	By H_2O_2	O	3·882
Bleaching powder	Chlorine	,,	O	1·5835
Potassium permanganate	Oxygen	,,	O	0·715
Chili saltpetre....	Sodium nitrate	Nitrometer	NO	3·805
Nitrous bodies ..	N_2O_3	,,	NO	1·701
,, ,,	HNO_3	,,	NO	2·820
,, ,,	Nitric acid 36° B.	,,	NO	5·330
,, ,,	Sodium nitrate	,,	NO	3·805
Nitroglycerol, dynamite, etc.....	Trinitroglycerol	,,	NO	3·387
,, ,,	Nitrogen	,,	NO	0·6267
Nitrocellulose, pyroxylin	,,	,,	NO	0·6267

* The corrections above referred to have here already been made.

Japp* describes a modification of Lunge's gas-volumeter, by means of which with accurately graduated ordinary 50 c.c. gas burettes any required single gas may without observation of temperature or pressure, and without calculation, be measured under such conditions that each c.c. represents a milligram of the gas. The name "gravivolumeter" is appropriately given to this instrument, and it undoubtedly possesses this advantage over Lunge's instrument that it obviates the necessity of having a number of different gas-volumeters for different substances, and moreover its manufacture involves no large amount of skill, as the ordinary graduation in c.c. in $\frac{1}{10}$ or $\frac{1}{20}$ is all that is required.

The apparatus is represented in fig. 121. It consists of two gas burettes, of 50 c.c. capacity each, both furnished with obliquely bored taps. One of these burettes, A, which has a three-way tap, is the gas measuring tube; the other, B, which need only have a single tap, performs the function of the regulator in Lunge's gas-volumeter, and may be termed the "regulator tube." As in Lunge's instrument, both tubes are moistened internally with a drop of water, in order that the gases they contain may be saturated with aqueous vapour, and both are connected, by means of stout, flexible tubing and a T-piece, with the *same* movable reservoir of mercury, C. And since, in certain determinations, the level of the mercury reservoir is considerably below the lower end of the two burettes, and an inward leakage of air might thus occur at the junctions of the burettes with the india-rubber tubing, these junctions are surrounded with pieces of wider india-rubber tubing, D, D, tied round the bottom and open at the top, and filled with water, so as to form a water joint.

The 25 c.c. division of the regulator tube is taken as the starting point in

* *J. C. S.* **59**, 894.

calculating what may be termed the "gravivolumetric values" of the different gases to be measured. Thus in the case of nitrogen it is necessary to calculate to what volume 25 c.c. of standard dry nitrogen must be brought in order that 1 c.c. may correspond with 1 mgm. of the gas; that is to say, 25 c.c. of standard dry nitrogen weigh $0.0012507 \times 25 = 0.0313$ gm.; and, therefore, these 31·3 mgm. must be brought to the volume of 31·3 c.c. The division 31·3 on the *regulator* tube is marked N_2. Corresponding points are in like manner determined for the various other gases which it is desired to measure, and these points are marked O_2, CO_2, etc., as the case may be, on the regulator tube. Finally, the thermometer and barometer are read (a process only necessary once for all in setting the regulator), the volume which 25 c.c. of standard dry air would occupy if measured moist at the observed temperature and pressure is calculated, and this calculated volume of air is admitted at atmospheric temperature and pressure into the regulator tube and the tap closed. The instrument is now ready for use.

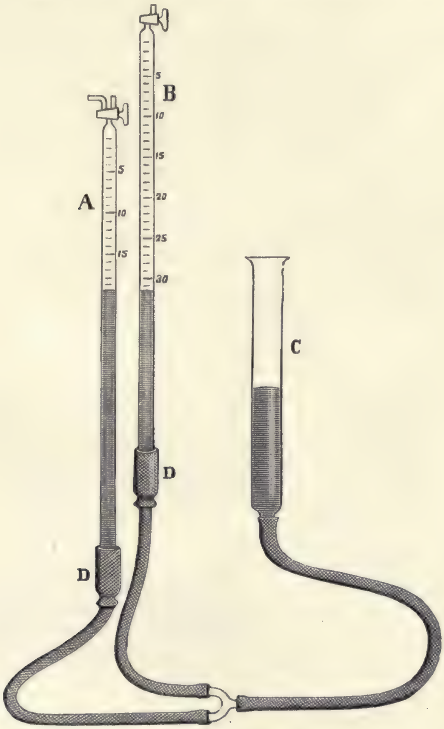


Fig. 121.

Suppose it is desired to ascertain the weight of a quantity of nitrogen contained in the measuring tube. The mercury reservoir is raised or lowered until the mercury in the regulator tube stand at the nitrogen mark, 31·3, at the same time adjusting the regulator tube itself by raising or lowering it bodily, so that the mercury level in the measuring tube and the regulator tube may be the same. *In these circumstances each cubic centimetre of gas in the measuring tube represents 1 mgm. of nitrogen.* For since in the regulator tube 25 c.c. of standard dry air have been made to occupy the volume of 31·3 c.c., and since the gases in the two tubes are under the same conditions as regards temperature, pressure, and saturation with aqueous vapour, therefore, in the measuring tube, every 25 c.c.

of standard dry nitrogen have also been made to occupy the volume of 31·3 c.c. But 25 c.c. of standard dry nitrogen weigh, as we have seen, 31·3 mgm. ; so that the problem is solved, and the cubic centimetres and tenths of cubic centimetres give directly the weight of the gas in milligrams and tenths of milligrams.

The various other single (*i.e.*, unmixed) gases may be weighed in like manner by bringing the mercury in the regulator tube to the "gravivolumetric mark" of the gas in question, and adjusting the levels as before. An exception would be made in the case of hydrogen, which would be brought to such a volume that the cubic centimetre would contain a *tenth* of a milligram.

Mixtures of gases may also be weighed, provided that the density of the mixture is known.

Lastly, if the mercury in the regulator tube be brought to the mark 25 and the levels adjusted, a gas or mixture of gases in the measuring tube will have the volume which it would occupy in the standard dry state. In this form the instrument is merely a gas-volumeter, as described by Lunge, and may be used for ordinary gas analysis.

The experiments made by Japp with the view of ascertaining the degree of accuracy of which the apparatus is capable were very satisfactory, details being given in the paper mentioned. The substances experimented on were Methane, with a gravivolumetric value of 17·9 ; Nitrogen, 31·3 ; Air, 32·35 ; and Carbon dioxide, 49·4

The measuring tube and regulator tube were held by a double clamp, the arms of which could be moved horizontally, so as to admit of bringing the tubes close together when necessary. The two tubes were so arranged that, after adjusting the levels and ascertaining that the mercury in the regulator tube was at the gravivolumetric mark, it was possible to read both levels without moving the position of the eye. The object of this was that any possible error of parallax might operate equally and in the same direction in both tubes, in which case the two errors would tend to neutralize one another in the final result.* The mercury reservoir was held by a clamp attached to a separate stand, so that in the case of extreme differences of pressure the entire stand could be placed on a different level from the rest of the apparatus.

Assuming the graduation of a gravivolumeter to be correct, or the defects of graduation to be eliminated by calibration, the sources of error in such an instrument are, broadly speaking, four in number, and are to be found in imperfections (1) in filling the regulator, (2) in adjusting the levels, (3) in reading the regulator, and (4) in reading the measuring tube. The first of these operations, that of filling the regulator, is performed once for all with very great care, and may, for all practical purposes, be disregarded as a source of error. Again, in adjusting the levels, the two tubes can be brought, by means of the double clamp, within such a short distance of one another that the adjustment is also practically accurate. The real sources of error lie in the last two operations. The burettes are divided into tenths of cubic centimetres, and can be read with the eye alone accurately to $\frac{1}{20}$ c.c. Calculating this error on 25 c.c. as the average volume of gas contained in the regulator tube and measuring the tube respectively, we have $1/(20 \times 25) = \frac{1}{500}$ as the error for each tube. But as the error in the regulator repeats itself in exact proportion in the altered volume of gas in the measuring tube, we must add the error of the regulator to the independent error of the measuring tube, in order to ascertain the maximum error, which would thus be $\frac{1}{250}$; and this, calculated as assumed, upon 25 c.c. of gas, would be equal to an error of reading 0·1 c.c. in the final result. An inspection of the foregoing experi-

* Suppose the eye in reading to be too high, the mercury in the regulator would stand *below* the gravivolumetric mark, and the gas in the measuring tube would consequently be expanded beyond its proper volume. But owing to the eye being too high, this too great volume in the measuring tube would be read off as smaller than it actually is. In the case of equal volumes of gas in regulator and measuring tube, there would thus be a total correction of the error committed (since the two tubes are of equal bore), and in every case a diminution.

mental results, however, discloses the fact that the maximum error is only half this amount, or 0·05 c.c.; and this the author attributes to the fact that, owing to the method of reading employed, the errors of reading in the regulator and measuring tube are not, as assumed in the foregoing calculation, independent, but tend to neutralize one another.

This error of 0·05 c.c. is, however, the error of reading of any gas burette which is read with the eye alone; and the gravivolumeter may, therefore, claim to possess the same degree of accuracy as instruments of this class generally.

TABLE 1.

Elasticity of Aqueous Vapour for each $\frac{1}{10}$th degree centigrade from 0° to 30° C. (Regnault).

Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres. of Mercury.	Temp. C.	Tension in Millimetres of Mercury.
·0°	4·6	6·0°	7·0	12·0°	10·5	18·0°	15·4	24·0°	22·2
·1	4·6	·1	7·0	·1	10·5	·1	15·5	·1	22·3
·2	4·7	·2	7·1	·2	10·6	·2	15·6	·2	22·5
·3	4·7	·3	7·1	·3	10·7	·3	15·7	·3	22·6
·4	4·7	·4	7·2	·4	10·7	·4	15·7	·4	22·7
·5	4·8	·5	7·2	·5	10·8	·5	15·8	·5	22·9
·6	4·8	·6	7·3	·6	10·9	·6	15·9	·6	23·0
·7	4·8	·7	7·3	·7	10·9	·7	16·0	·7	23·1
·8	4·9	·8	7·4	·8	11·0	·8	16·1	·8	23·3
·9	4·9	·9	7·4	·9	11·1	·9	16·2	·9	23·4
1·0	4·9	7·0	7·5	13·0	11·2	19·0	16·3	25·0	23·5
·1	5·0	·1	7·5	·1	11·2	·1	16·4	·1	23·7
·2	5·0	·2	7·6	·2	11·3	·2	16·6	·2	23·8
·3	5·0	·3	7·6	·3	11·4	·3	16·7	·3	24·0
·4	5·1	·4	7·7	·4	11·5	·4	16·8	·4	24·1
·5	5·1	·5	7·8	·5	11·5	·5	16·9	·5	24·3
·6	5·2	·6	7·8	·6	11·6	·6	17·0	·6	24·4
·7	5·2	·7	7·9	·7	11·7	·7	17·1	·7	24·6
·8	5·2	·8	7·9	·8	11·8	·8	17·2	·8	24·7
·9	5·3	·9	8·0	·9	11·8	·9	17·3	·9	24·8
2·0	5·3	8·0	8·0	14·0	11·9	20·0	17·4	26·0	25·0
·1	5·3	·1	8·1	·1	12·0	·1	17·5	·1	25·1
·2	5·4	·2	8·1	·2	12·1	·2	17·6	·2	25·3
·3	5·4	·3	8·2	·3	12·1	·3	17·7	·3	25·4
·4	5·5	·4	8·2	·4	12·2	·4	17·8	·4	25·6
·5	5·5	·5	8·3	·5	12·3	·5	17·9	·5	25·7
·6	5·5	·6	8·3	·6	12·4	·6	18·0	·6	25·9
·7	5·6	·7	8·4	·7	12·5	·7	18·2	·7	26·0
·8	5·6	·8	8 5	·8	12·5	·8	18·3	·8	26·2
·9	5·6	·9	8.5	·9	12·6	·9	18·4	·9	26·4
3·0	5·7	9·0	8·6	15·0	12·7	21·0	18·5	27·0	26·5
·1	5·7	·1	8·6	·1	12·8	·1	18·6	·1	26·7
·2	5·8	·2	8·7	·2	12·9	·2	18·7	·2	26·8
·3	5·8	·3	8·7	·3	12·9	·3	18·8	·3	27·0
·4	5·8	·4	8·8	·4	13·0	·4	19·0	·4	27·1
·5	5·9	·5	8·9	·5	13·1	·5	19·1	·5	27·3
·6	5·9	·6	8·9	·6	13·2	·6	19·2	·6	27·5
·7	6·0	·7	9·0	·7	13·3	·7	19·3	·7	27·6
·8	6·0	·8	9·0	·8	13·4	·8	19·4	·8	27·8
·9	6·1	·9	9·1	·9	13·5	·9	19·5	·9	27·9
4·0	6·1	10·0	9·2	16·0	13·5	22·0	19·7	28·0	28·1
·1	6·1	·1	9·2	·1	13·6	·1	19·8	·1	28·3
·2	6·2	·2	9·3	·2	13·7	·2	19·9	·2	28·4
·3	6·2	·3	9·3	·3	13·8	·3	20·0	·3	28·6
·4	6·3	·4	9·4	·4	13·9	·4	20·1	·4	28·8
·5	6·3	·5	9·5	·5	14·0	·5	20·3	·5	28·9
·6	6·4	·6	9·5	·6	14·1	·6	20·4	·6	29·1
·7	6·4	·7	9·6	·7	14·2	·7	20·5	·7	29·3
·8	6·4	·8	9·7	·8	14·2	·8	20·6	·8	29·4
·9	6·5	·9	9·7	·9	14·3	·9	20·8	·9	29·6
5·0	6·5	11·0	9·8	17·0	14·4	23·0	20·9	29·0	29·8
·1	6·6	·1	9·9	·1	14·5	·1	21·0	·1	30·0
·2	6·6	·2	9·9	·2	14·6	·2	21·1	·2	30·1
·3	6·7	·3	10·0	·3	14·7	·3	21·3	·3	30·3
·4	6·7	·4	10·1	·4	14·8	·4	21·4	·4	30·5
·5	6·8	·5	10·1	·5	14·9	·5	21·5	·5	30·7
·6	6·8	·6	10·2	·6	15·0	·6	21·7	·6	30·8
·7	6·9	·7	10·3	·7	15·1	·7	21·8	·7	31·0
·8	6·9	·8	10·3	·8	15·2	·8	21·9	·8	31·2
·9	7·0	·9	10·4	·9	15·3	·9	22·1	·9	31·4

TABLE 2.

Reduction of Cubic Centimetres of Nitrogen to Grams.

Log. $\frac{0 \cdot 0012562}{(1 + 0 \cdot 00367t)760}$ for each tenth of a degree from 0° to 30° C.

t. C.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0°	$\bar{6}$·21824	808	793	777	761	745	729	713	697	681
1	665	649	633	617	601	586	570	554	538	522
2	507	491	475	459	443	427	412	396	380	364
3	349	333	318	302	286	270	255	239	223	208
4	192	177	161	145	130	114	098	083	067	051
5	035	020	004	*989	*973	*957	*942	*926	*911	*895
6	$\bar{6}$·20879	864	848	833	817	801	786	770	755	739
7	723	708	692	676	661	645	629	614	598	583
8	567	552	536	521	505	490	474	459	443	428
9	413	397	382	366	351	335	320	304	289	274
10	259	244	228	213	198	182	167	151	136	121
11	106	090	075	060	045	029	014	*999	*984	*969
12	$\bar{6}$·19953	938	923	907	892	877	862	846	831	816
13	800	785	770	755	740	724	709	694	679	664
14	648	633	618	603	588	573	558	543	528	513
15	497	482	467	452	437	422	407	392	377	362
16	346	331	316	301	286	271	256	241	226	211
17	196	181	166	151	136	121	106	091	076	061
18	046	031	016	001	*986	*971	*956	*941	*926	*911
19	$\bar{6}$·18897	882	867	852	837	822	807	792	777	762
20	748	733	718	703	688	673	659	644	629	614
21	600	585	570	555	540	526	511	496	481	466
22	452	437	422	408	393	378	363	349	334	319
23	305	290	275	261	246	231	216	202	187	172
24	158	143	128	114	099	084	070	055	041	026
25	012	*997	*982	*968	*953	*938	*924	*909	*895	*880
26	$\bar{6}$·17866	851	837	822	808	793	779	764	750	735
27	721	706	692	677	663	648	634	619	605	590
28	576	561	547	532	518	503	489	475	460	446
29	432	417	403	388	374	360	345	331	316	302

TABLE 3.

Loss of Nitrogen by Evaporation of NH^3.
With Sulphurous Acid.

Parts per 100,000.

N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3.	Loss of N.
5·0	1·741	3·9	1·425	2·8	·898	1·7	·370	·6	·145	·04	·009
4·9	1·717	3·8	1·378	2·7	·850	1·6	·338	·5	·109	·03	·007
4·8	1·693	3·7	1·330	2·6	·802	1·5	·324	·4	·075	·02	·005
4·7	1·669	3·6	1·282	2·5	·754	1·4	·309	·3	·057	·01	·003
4·6	1·645	3·5	1·234	2·4	·706	1·3	·295	·2	·038	·008	·002
4·5	1·621	3·4	1·186	2·3	·658	1·2	·280	·1	·020	·007	·001
4·4	1·598	3·3	1·138	2·2	·610	1·1	·266	·09	·018		
4·3	1·574	3·2	1·090	2·1	·562	1·0	·252	·08	·017		
4·2	1·550	3·1	1·042	2·0	·514	·9	·237	·07	·015		
4·1	1·521	3·0	·994	1·9	·466	·8	·217	·06	·013		
4·0	1·473	2·9	·946	1·8	·418	·7	·181	·05	·011		

TABLE 4.

Loss of Nitrogen by Evaporation of NH^3.
With Hydric Metaphosphate.

Parts per 100,000.

Volume evaporated.	N as NH^3.	Loss of N.	Volume evaporated.	N as NH^3.	Loss of N.	Volume evaporated.	N as NH^3.	Loss of N.	Volume evaporated.	N as NH^3.	Loss of N.
100 c.c.	8·2	·482	100 c.c.	5·9	·385	100 c.c.	3·6	·281	100 c.c.	1·3	·142
..	8·1	·477	..	5·8	·381	..	3·5	·277	..	1·2	·136
..	8·0	·473	..	5·7	·377	..	3·4	·272	..	1·1	·129
..	7·9	·469	..	5·6	·373	..	3·3	·267	..	1·0	·123
..	7·8	·465	..	5·5	·368	..	3·2	·261	..	·9	·117
..	7·7	·461	..	5·4	·364	..	3·1	·255	..	·8	·111
..	7·6	·456	..	5·3	·360	..	3·0	·249	250 c.c.	·7	·088
..	7·5	·452	..	5·2	·356	..	2·9	·242	..	·6	·073
..	7·4	·448	..	5·1	·352	..	2·8	·236	..	·5	·061
..	7·3	·444	..	5·0	·347	..	2·7	·230	500 c.c.	·4	·049
..	7·2	·440	..	4·9	·343	..	2·6	·223	..	·3	·036
..	7·1	·435	..	4·8	·338	..	2·5	·217	1000 c.c.	·2	·024
..	7·0	·431	..	4·7	·334	..	2·4	·211	..	·1	·012
..	6·9	·427	..	4·6	·329	..	2·3	·205	..	·09	·011
..	6·8	·423	..	4·5	·324	..	2·2	·198	..	·08	·010
..	6·7	·419	..	4·4	·319	..	2·1	·192	..	·07	·008
..	6·6	·414	..	4·3	·315	..	2·0	·186	..	·06	·007
..	6·5	·410	..	4·2	·310	..	1·9	·180	..	·05	·006
..	6·4	·406	..	4·1	·305	..	1·8	·173	..	·04	·005
..	6·3	·402	..	4·0	·301	..	1·7	·167	..	·03	·004
..	6·2	·398	..	3·9	·296	..	1·6	·161	..	·02	·002
..	6·1	·394	..	3·8	·291	..	1·5	·154	..	·01	·001
..	6·0	·389	..	3·7	·286	..	1·4	·148			

TABLE 5.

Loss of Nitrogen by Evaporation of NH^3.
With Sulphurous Acid.

Parts per 100,000.

NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3.	Loss of N.
6·0	1·727	4·8	1·451	3·6	·977	2·4	·503	1·2	·250	·09	·014
5·9	1·707	4·7	1·411	3·5	·937	2·3	·463	1·1	·238	·08	·013
5·8	1·688	4·6	1·372	3·4	·898	2·2	·424	1·0	·226	·07	·012
5·7	1·668	4·5	1·332	3·3	·858	2·1	·384	·9	·196	·06	·010
5·6	1·648	4·4	1·293	3·2	·819	2·0	·345	·8	·166	·05	·009
5·5	1·628	4·3	1·253	3·1	·779	1·9	·333	·7	·136	·04	·007
5·4	1·609	4·2	1·214	3·0	·740	1·8	·321	·6	·106	·03	·006
5·3	1·589	4·1	1·174	2·9	·700	1·7	·309	·5	·077	·02	·004
5·2	1·569	4·0	1·135	2·8	·661	1·6	·297	·4	·062	·01	·003
5·1	1·549	3·9	1·095	2·7	·621	1·5	·285	·3	·047	·009	·001
5·0	1·530	3·8	1·056	2·6	·582	1·4	·274	·2	·032		
4·9	1·490	3·7	1·016	2·5	·542	1·3	·262	·1	·017		

TABLE 6.

Loss of Nitrogen by Evaporation of NH^3.
With Hydric Metaphosphate.

Parts per 100,000.

Volume evaporated.	NH^3.	Loss of N.	Volume evaporated.	NH^3.	Loss of N.	Volume evaporated.	NH^3.	Loss of N.	Volume evaporated.	NH^3.	Loss of N.
100 c.c.	10·0	·483	100 c.c.	7·2	·386	100 c.c.	4·4	·283	100 c.c.	1·6	·143
..	9·9	·480	..	7·1	·382	..	4·3	·279	..	1·5	·137
..	9·8	·476	..	7·0	·379	..	4·2	·275	..	1·4	·132
..	9·7	·473	..	6·9	·375	..	4·1	·271	..	1·3	·127
..	9·6	·469	..	6·8	·372	..	4·0	·267	..	1·2	·122
..	9·5	·466	..	6·7	·368	..	3·9	·262	..	1·1	·117
..	9·4	·462	..	6·6	·365	..	3·8	·257	..	1·0	·112
..	9·3	·459	..	6·5	·361	..	3·7	·252	250 c.c.	·9	·096
..	9·2	·455	..	6·4	·358	..	3·6	·247	..	·8	·080
..	9·1	·452	..	6·3	·354	..	3·5	·242	..	·7	·070
..	9·0	·448	..	6·2	·351	..	3·4	·236	..	·6	·060
..	8·9	·445	..	6·1	·348	..	3·3	·231	500 c.c.	·5	·050
..	8·8	·441	..	6·0	·345	..	3·2	·226	..	·4	·040
..	8·7	·438	..	5·9	·341	..	3·1	·221	..	·3	·030
..	8·6	·434	..	5·8	·337	..	3·0	·216	1000 c.c.	·2	·020
..	8·5	·431	..	5·7	·333	..	2·9	·211	..	·1	·010
..	8·4	·428	..	5·6	·330	..	2·8	·205	..	·09	·009
..	8·3	·424	..	5·5	·326	..	2·7	·200	..	·08	·008
..	8·2	·421	..	5·4	·322	..	2·6	·195	..	·07	·007
..	8·1	·417	..	5·3	·318	..	2·5	·190	..	·06	·006
..	8·0	·414	..	5·2	·314	..	2·4	·184	..	·05	·005
..	7·9	·410	..	5·1	·310	..	2·3	·179	..	·04	·004
..	7·8	·407	..	5·0	·306	..	2·2	·174	..	·03	·003
..	7·7	·403	..	4·9	·302	..	2·1	·169	..	·02	·002
..	7·6	·400	..	4·8	·298	..	2·0	·164	..	·01	·001
..	7·5	·396	..	4·7	·294	..	1·9	·158			
..	7·4	·393	..	4·6	·291	..	1·8	·153			
..	7·3	·389	..	4·5	·287	..	1·7	·148			

TABLE 7.

Table of Hardness, Parts in 100,000.

Volume of Soap Solution.	$CaCO_3$ ⅌ 100,000.	Volume of Soap Solution.	$CaCO_3$ ⅌ 100,000.	Volume of Soap Solution.	$CaCO_3$ ⅌ 100,000.	Volume of Soap Solution.	$CaCO_3$ ⅌ 100,000.
c.c.		c.c.		c.c.		c.c.	
		4·0	4·57	8·0	10·30	12·0	16·43
		1	·71	1	·45	1	·39
		2	·86	2	·60	2	·75
		3	5·00	3	·75	3	·90
		4	·14	4	·90	4	17·06
		5	·29	5	11·05	5	·22
		6	·43	6	·20	6	·38
0·7	·00	7	·57	7	·35	7	·54
0·8	·16	8	·71	8	·50	8	·70
0·9	·32	9	·86	9	·65	9	·86
1·0	·48	5·0	6·00	9·0	·80	13·0	18·02
1	·63	1	·14	1	·95	1	·17
2	·79	2	·29	2	12·11	2	·33
3	·95	3	·43	3	·26	3	·49
4	1·11	4	·57	4	·41	4	·65
5	·27	5	·71	5	·56	5	·81
6	·43	6	·86	6	·71	6	·97
7	·56	7	7·00	7	·86	7	19·13
8	·69	8	·14	8	13·01	8	·29
9	·82	9	·29	9	·16	9	·44
2·0	·95	6·0	·43	10·0	·31	14·0	·60
1	2·08	1	·57	1	·46	1	·76
2	·21	2	·71	2	·61	2	·92
3	·34	3	·86	3	·76	3	20·08
4	·47	4	8·00	4	·91	4	·24
5	·60	5	·14	5	14·06	5	·40
6	·73	6	·29	6	·21	6	·56
7	·86	7	·43	7	·37	7	·71
8	·99	8	·57	8	·52	8	·87
9	3·12	9	·71	9	·68	9	21·03
3·0	·25	7·0	·86	11·0	·84	15·0	·19
1	·38	1	9·00	1	15·00	1	·35
2	·51	2	·14	2	·16	2	·51
3	·64	3	·29	3	·32	3	·68
4	·77	4	·43	4	·48	4	·85
5	·90	5	·57	5	·63	5	22·02
6	4·03	6	·71	6	·79	6	·18
7	·16	7	·86	7	·95	7	·35
8	·29	8	10·00	8	16·11	8	·52
3·9	·43	7·9	·15	11·9	·27	9	·69
						16·0	·86

TABLE 8.

Oxygen Dissolved by Distilled Water. 5–30° C.

(Roscoe and Lunt).*

Temp. C.	c.c. Oxygen N.T.P. per litre Aq.	Diff. for 0·5° C.	Temp. C.	c.c. Oxygen N.T.P. per litre Aq.	Diff. for 0·5° C.
5·0°	8·68		18·0°	6·54	0·07
5·5	8·58	0·10	18·5	6·47	0·07
6·0	8·49	0·09	19·0	6·40	0·06
6·5	8·40	0·09	19·5	6·34	0·06
7·0	8·31	0·09	20·0	6·28	0·06
7·5	8·22	0·09	20·5	6·22	0·06
8·0	8·13	0·09	21·0	6·16	0·06
8·5	8·04	0·09	21·5	6·10	0·06
9·0	7·95	0·09	22·0	6·04	0·05
9·5	7·86	0·09	22·5	5·99	0·05
10·0	7·77	0·09	23·0	5·94	0·05
10·5	7·68	0·08	23·5	5·89	0·05
11·0	7·60	0·08	24·0	5·84	0·04
11·5	7·52	0·08	24·5	5·80	0·04
12·0	7·44	0·08	25·0	5·76	0·04
12·5	7·36	0·08	25·5	5·72	0·04
13·0	7·28	0·08	26·0	5·68	0·04
13·5	7·20	0·08	26·5	5·64	0·04
14·0	7·12	0·08	27·0	5·60	0·03
14·5	7·04	0·08	27·5	5·57	0·03
15·0	6·96	0·08	28·0	5·54	0·03
15·5	6·89	0·07	28·5	5·51	0·03
16·0	6·82	0·07	29·0	5·48	0·03
16·5	6·75	0·07	29·5	5·45	0·02
17·0	6·68	0·07	30·0	5·43	
17·5	6·61	0·07			

In this table the results are calculated for aeration at an *observed* barometric pressure of 760 mm. When the observed pressure is *below* 760 mm. $\frac{1}{76}$ the value must be *subtracted* for every 10 mm. diff. The same value must be *added* when the pressure is *above* 760 mm.

* *J. C. S.* 1889, 532.

TABLE 9.

Amounts of Dissolved Oxygen in distilled Water from 0°-30° C. (Bar. 760 mm.).*

Temperature °C.	Oxygen (Parts per 100,000).	Temperature °C.	Oxygen (Parts per 100,000).
0	1·42	16	0·98
1	1·39	17	0·96
2	1·36	18	0·94
3	1·32	19	0·92
4	1·28	20	0·90
5	1·24	21	0·88
6	1·22	22	0·87
7	1·19	23	0·85
8	1·17	24	0·84
9	1·14	25	0·82
10	1·11	26	0·81
11	1·09	27	0·80
12	1·07	28	0·80
13	1·04	29	0·79
14	1·02	30	0·78
15	1·00	—	—

* Calculated from Roscoe and Lunt's table from 5°–30° C. and from determinations by Winkler's process for the values given for 0° to 4° C.

TABLE 9a.

Absorption coefficients of the Commoner Gases in Water at 15° C.

Propylene	0·237	Carbon dioxide	0·024
Ethylene	0·162	Hydrogen	0·019
Methane	0·039	Oxygen	0·030
Carbon dioxide	1·002	Nitrogen	0·015

More recent determinations by Winkler are as follows :—

Coefficient of Solubility at	10°	12°	14°	16°	18°	20°
Oxygen	0·038	0·036	0·035	0·033	0·032	0·031
Nitrogen	0·018	0·018	0·017	0·016	0·016	0·015
Hydrogen	0·020	0·019	0·019	0·019	0·018	0·018
Carbon monoxide	0·028					0·023

TABLE 10.

TABLE for Correction of Volumes of Gases for Temperature, according to the Formula $V^1 = \frac{V \times B}{760 \times (1 + \delta t)}$

$1 + \delta t$ from 0° to 30°. $\delta = 0·003665$.

t	$1 + \delta t$	Log. $(1 + \delta t)$	t	$1 + \delta t$	Log. $(1 + \delta t)$	t	$1 + \delta t$	Log. $(1 + \delta t)$
0°·0	1·0000000	0·000 0000	5°·0	1·0183250	0·007 8864	10°·0	1·0366500	0·015 6321
·1	1·0003665	1591	·1	1·0186915	0·008 0427	·1	1·0370165	7857
·2	1·0007330	3182	·2	1·0190580	1989	·2	1·0373830	9391
·3	1·0010995	4772	·3	1·0194245	4551	·3	1·0377495	0·016 0925
·4	1·0014660	6362	·4	1·0197910	5112	·4	1·0381160	2459
0·5	1·0018325	7951	5·5	1·0201575	6672	10·5	1·0384825	3992
·6	1·0021990	9540	·6	1·0205240	8232	·6	1·0388490	5524
·7	1·0025655	0·001 1128	·7	1·0208905	9791	·7	1·0392155	7056
·8	1·0029320	2715	·8	1·0212570	0·009 1350	·8	1·0395820	8588
·9	1·0032985	4302	5·9	1·0216235	2909	10·9	1·0399485	0·017 0118
1·0	1·0036650	0·001 5888	6·0	1·0219900	0·009 4466	11·0	1·0403150	0·017 1648
·1	1·0040315	7473	·1	1·0223565	6024	·1	1·0406815	3178
·2	1·0043980	9058	·2	1·0227230	7580	·2	1·0410480	4708
·3	1·0047645	0·002 0643	·3	1·0230895	9136	·3	1·0414145	6236
·4	1·0051310	2227	·4	1·0234560	0·010 0692	·4	1·0417810	7764
1·5	1·0054975	3810	6·5	1·0238225	2247	11·5	1·0421475	9292
·6	1·0058640	5393	·6	1·0241890	3801	·6	1·0425140	0·018 0819
·7	1·0062305	6974	·7	1·0245555	5355	·7	1·0428805	2346
·8	1·0065970	8556	·8	1·0249220	6908	·8	1·0432470	3871
1·9	1·0069635	0·003 0137	6·9	1·0252885	8461	11·9	1·0436135	5397
2·0	1·0073300	0·003 1718	7·0	1·0256550	0·011 0013	12·0	1·0439800	0·018 6922
·1	1·0076965	3298	·1	1·0260215	1565	·1	1·0443465	8446
·2	1·0080630	4877	·2	1·0263880	3116	·2	1·0447130	9970
·3	1·0084295	6455	·3	1·0267545	4666	·3	1·0450795	0·019 1493
·4	1·0087960	8033	·4	1·0271210	6216	·4	1·0454460	3016
2·5	1·0091625	9611	7·5	1·0274875	7765	12·5	1·0458125	4538
·6	1·0095290	0·004 1188	·6	1·0278540	9314	·6	1·0461790	6060
·7	1·0098955	2764	·7	1·0282205	0·012 0863	·7	1·0465455	7581
·8	1·0102620	4340	·8	1·0285870	2410	·8	1·0469120	9102
2·9	1·0106285	5916	7·9	1·0289535	3957	12·9	1·0472785	0·020 0622
3·0	1·0109950	0·004 7490	8·0	1·0293200	0·012 5504	13·0	1·0476450	0·020 2141
·1	1·0113615	9064	·1	1·0296865	7050	·1	1·0480115	3660
·2	1·0117280	0·005 0638	·2	1·0300530	8596	·2	1·0483780	5179
·3	1·0120945	2211	·3	1·0304195	0·013 0141	·3	1·0487445	6697
·4	1·0124610	3783	·4	1·0307860	1685	·4	1·0491110	8214
3·5	1·0128275	5355	8·5	1·0311525	3229	13·5	1·0494775	9731
·6	1·0131940	6926	·6	1·0315190	4772	·6	1·0498440	0·021 1248
·7	1·0135605	8497	·7	1·0318855	6315	·7	1·0502105	2764
·8	1·0139270	0·006 0067	·8	1·0322520	7857	·8	1·0505770	4279
3·9	1·0142935	1636	8·9	1·0326185	9399	13·9	1·0509435	5794
4·0	1·0146600	0·006 3205	9·0	1·0329850	0·014 0940	14·0	1·0513100	0·021 7308
·1	1·0150265	4774	·1	1·0333515	2481	·1	1·0516765	8822
·2	1·0153930	6342	·2	1·0337180	4021	·2	1·0520430	0·022 0335
·3	1·0157595	7909	·3	1·0340845	5560	·3	1·0524095	1848
·4	1·0161260	9476	·4	1·0344510	7099	·4	1·0527760	3360
4·5	1·0164925	0·007 1042	9·5	1·0348175	8638	14·5	1·0531425	4871
·6	1·0168590	2607	·6	1·0351840	0·015 0175	·6	1·0535090	6382
·7	1·0172255	4172	·7	1·0355505	1713	·7	1·0538755	7893
·8	1·0175920	5737	·8	1·0359170	3250	·8	1·0542420	9403
4·9	1·0179585	7301	9·9	1·0362835	4786	14·9	1·0546085	0·023 0193

TABLE 10 (*continued*).

TABLE for Correction of Volumes of Gases—*continued.*

t	$1+\delta t$	Log. $(1+\delta t)$	t	$1+\delta t$	Log. $(1+\delta t)$	t	$1+\delta t$	Log. $(1+\delta t)$
15·0°	1·0549750	0·023 2422	20·0°	1·0730000	0·030 7211	25·0°	1·0916250	0·038 0734
·1	1·0553415	3930	·1	1·0736665	8694	·1	1·0919915	2192
·2	1·0557080	5438	·2	1·0740330	0·031 0176	·2	1·0923580	3650
·3	1·0560745	6946	·3	1·0743995	1658	·3	1·0927245	5107
·4	1·0564410	8452	·4	1·0747660	3139	·4	1·0930910	6563
15·5	1·0568075	9959	20·5	1·0751325	4620	25·5	1·0934575	8020
·6	1·0571740	0·024 1465	·6	1·0754990	6100	·6	1·0938240	9474
·7	1·0575405	2970	·7	1·0758655	7580	·7	1·0941905	0·039 0929
·8	1·0579070	4475	·8	1·0762320	9059	·8	1·0945570	2384
15·9	1·0582735	5979	20·9	1·0765985	0·032 0538	·9	1·0949235	3838
16·0	1·0586400	0·024 7483	21·0	1·0769650	0·032 2016	26·0	1·0952900	0·039 5291
·1	1·0590065	8986	·1	1·0773315	3493	·1	1·0956565	6745
·2	1·0593730	0·025 0489	·2	1·0776980	4971	·2	1·0960230	8197
·3	1·0597395	1991	·3	1·0780645	6447	·3	1·0963895	9649
·4	1·0601060	3493	·4	1·0784310	7924	·4	1·0967560	0·040 1101
16·5	1·0604725	4994	21·5	1·0787975	9399	26·5	1·0971225	2551
·6	1·0608390	6495	·6	1·0791640	0·033 0874	·6	1·0974890	4002
·7	1·0612055	7995	·7	1·0795305	2349	·7	1·0978555	5452
·8	1·0615720	9495	·8	1·0798970	3823	·8	1·0982220	6901
16·9	1·0619385	0·026 0994	21·9	1·0802635	5298	·9	1·0985885	8351
17·0	1·0623050	0·026 2492	22·0	1·0806300	0·033 6771	27·0	1·0989550	0·040 9800
·1	1·0626715	3990	·1	1·0809965	8243	·1	1·0993215	0·041 1247
·2	1·0630380	5488	·2	1·0813630	9715	·2	1·0996880	2695
·3	1·0634045	6985	·3	1·0817295	0·034 1186	·3	1·1000545	4143
·4	1·0637710	8482	·4	1·0820960	2658	·4	1·1004210	5589
17·5	1·0641375	9978	22·5	1·0824625	4129	27·5	1·1007875	7036
·6	1·0645040	0·027 1473	·6	1·0828290	5598	·6	1·1011540	8481
·7	1·0648705	2968	·7	1·0831955	7069	·7	1·1015205	9926
·8	1·0652370	4462	·8	1·0835620	8538	·8	1·1018870	0·042 1371
17·9	1·0656035	5956	22·9	1·0839285	0·035 0006	·9	1·1022535	2815
18·0	1·0659700	0·027 7450	23·0	1·0842950	0·035 1475	28·0	1·1026200	0·042 4259
·1	1·0663365	8943	·1	1·0846615	2942	·1	1·1029865	5703
·2	1·0667030	0·028 0435	·2	1·0850280	4409	·2	1·1033530	7145
·3	1·0670695	1927	·3	1·0853945	5876	·3	1·1037195	8587
·4	1·0674360	3418	·4	1·0857610	7342	·4	1·1040860	0·043 0029
18.5	1·0678025	4909	23·5	1·0861275	8808	28·5	1·1044525	1471
·6	1.0681690	6400	·6	1·0864940	0·036 0273	·6	1·1048190	2911
·7	1·0685355	7889	·7	1·0868605	1738	·7	1·1051855	4352
·8	1·0689020	9379	·8	1 0872270	3202	·8	1·1055520	5792
18·9	1·0692685	0·029 0868	23·9	1·0875935	4666	·9	1·1059185	7231
19·0	1·0696350	0·029 2356	24·0	1·0879600	0·036 6129	29·0	1·1062850	0·043 8671
·1	1·0700015	3844	·1	1·0883265	7592	·1	1·1066515	0·044 0109
·2	1·0703680	5331	·2	1·0886930	9054	·2	1·1070180	1546
·3	1·0707345	6818	·3	1·0890595	0·037 0517	·3	1·1073845	2985
·4	1·0711010	8304	·4	1·0894260	1978	·4	1·1077510	4422
19·5	1·0714675	9790	24·5	1·0897925	3438	29·5	1·1081175	5858
·6	1·0718340	0·030 1275	·6	1·0901590	4899	·6	1·1084840	7295
·7	1·0722005	2760	·7	1·0905255	6359	·7	1·1088505	8730
·8	1·0725670	4244	·8	1·0908920	7817	·8	1·1092170	0·045 0165
19·9	1·0729335	5728	·9	1·0912585	9277	·9	1·1095835	1600
						30·0	1·1099500	0·045 3035

TABLE 11.

TABLE for Correction of Volumes of Gases for Temperature, giving the Divisor for the Formula

$$V^1 = \frac{V \times B}{760 \times (1 + \delta t)}.$$

t	760 × (1 + δt).	Log. [760 × (1 + δt)].	t	760 × (1 + δt).	Log. [760 × (1 + δt)].	t	760 × (1 + δt).	Log. [760 × (1 + δt)].
0·0	760·0000	2·880 8136	4·0	771·1416	2·887 1341	8·0	782·2832	2·893 3640
·1	760·2785	9727	·1	771·4201	2910	·1	782·5617	5186
·2	760·5571	2·881 1319	·2	771·6987	4478	·2	782·8403	6732
·3	760·8356	2908	·3	771·9772	6044	·3	783·1188	8276
·4	761·1142	4498	·4	772·2558	7611	·4	783·3974	9821
0·5	761·3927	6087	4·5	772·5343	9178	8·5	783·6759	2·894 1365
·6	761·6712	7676	·6	772·8128	2·888 0743	·6	783·9544	2908
·7	761·9498	9264	·7	773·0914	2309	·7	784·2330	4452
·8	762·2283	2·882 0851	·8	773·3699	3872	·8	784·5115	5994
·9	762·5069	2437	·9	773·6485	5437	·9	784·7901	7536
1·0	762·7854	2·882 4024	5·0	773·9270	2·888 7000	9·0	785·0686	2·894 9076
·1	763·0639	5610	·1	774·2055	8563	·1	785·3471	2·895 0617
·2	763·3425	7194	·2	774·4841	2·889 0125	·2	785·6257	2157
·3	763·6210	8779	·3	774·7626	1686	·3	785·9042	3696
·4	763·8996	2·883 0362	·4	775·0412	3248	·4	786·1828	5235
1·5	764·1781	1947	5·5	775·3197	4808	9·5	786·4613	6774
·6	764·4566	3528	·6	775·5982	6368	·6	786·7398	8311
·7	764·7352	5111	·7	775·8768	7927	·7	787·0184	9849
·8	765·0137	6692	·8	776·1553	9487	·8	787·2969	2·896 1385
·9	765·2923	8273	·9	776·4339	2·890 1044	·9	787·5755	2923
2·0	765·5708	2·883 9854	6·0	776·7124	2·890 2602	10·0	787·8540	2·896 4457
·1	765·8493	2·884 1433	·1	776·9909	4159	·1	788·1325	5993
·2	766·1279	3013	·2	777·2695	5716	·2	788 4111	7528
·3	766·4064	4591	·3	777·5480	7272	·3	788·6896	9061
·4	766·6850	6170	·4	777·8266	8828	·4	788·9682	2·897 0595
2·5	766·9635	7747	6·5	778·1051	2·891 0383	10·5	789·2467	2128
·6	767·2420	9323	·6	778·3836	1937	·6	789·5252	3660
·7	767·5206	2·885 0900	·7	778·6622	3491	·7	789·8038	5192
·8	767·7991	2476	·8	778·9407	5044	·8	790·0823	6724
·9	768·0777	4052	·9	779·2193	6597	·9	790·3609	8255
3·0	768·3562	2·885 5626	7·0	779·4978	2·891 8149	11·0	790·6394	2·897 9785
·1	768·6347	7200	·1	779·7763	9701	·1	790·9179	2·898 1315
·2	768·9133	8772	·2	780·0549	2·892 1251	·2	791·1965	2844
·3	769·1918	2·886 0347	·3	780·3334	2802	·3	791·4750	4373
·4	769·4704	1919	·4	780·6120	4352	·4	791·7536	5901
3·5	769·7489	3491	7·5	780·8905	5901	11·5	792·0321	7428
·6	770·0274	5061	·6	781·1690	7450	·6	792·3106	8954
·7	770·3060	6633	·7	781·4476	8998	·7	792 5892	2·899 0482
·8	770·5845	8203	·8	781·7261	2·893 0547	·8	792·8677	2008
·9	770·8631	9773	·9	782·0047	2094	·9	793·1463	3534

TABLE 11 (*continued*).

TABLE for Correction of Volumes of Gases—*continued.*

t	$760 \times (1+\delta t)$.	Log. $[760 \times (1+\delta t)]$.	t	$760 \times (1+\delta t)$.	Log. $[760 \times (1+\delta t)]$.	t	$760 \times (1+\delta t)$.	Log. $[760 \times (1+\delta t)]$.
12·0	793·4248	2·899 5057	16·5	805·9591	2·906 3131	21·0	818·4934	2·913 0152
·1	793·7033	6583	·6	806·2376	4630	·1	818·7719	1629
·2	793·9819	8106	·7	806·5162	6131	·2	819·0505	3107
·3	794·2604	9629	·8	8[illegible]6·7947	7631	·3	819·3290	4584
·4	794·5390	2·900 1153	·9	807·0733	9130	·4	819·6076	6059
12·5	794·8175	2674	17·0	807·3518	2·907 0627	21·5	819·8861	7535
·6	795·0960	4196	·1	807·6303	2126	·6	820·1646	9010
·7	795·3746	5717	·2	807·9089	3624	·7	820·4432	2·914 0485
·8	795·6531	7238	·3	808·1874	5121	·8	820·7217	1959
·9	795·9317	8758	·4	808·4660	6617	21·9	821·0003	3434
13·0	796·2102	2·901 0277	17·5	808·7445	8114	22·0	821·2788	2·914 4906
·1	796·4887	1796	·6	809·0230	9609	·1	821·5573	6379
·2	796·7673	3316	·7	809·3016	2·908 1103	·2	821·8359	7852
·3	797·0458	4833	·8	809·5801	2599	·3	822·1144	9322
·4	797·3244	6351	·9	809·8587	4092	·4	822·3930	2·915 0794
13·5	797·6029	7867	18·0	810·1372	2·908 5586	22·5	822·6715	2265
·6	797·8814	9383	·1	810·4157	7079	·6	822·9500	3734
·7	798·1600	2·902 0900	·2	810·6943	8572	·7	823·2286	5204
·8	798·4385	2415	·3	810·9728	2·909 0063	·8	823·5071	6674
·9	798·7171	3931	·4	811·2514	1554	·9	823·7857	8143
14·0	798·9956	2·902 5444	18·5	811·5299	3046	23·0	824·0642	2·915 9610
·1	799·2741	6958	·6	811·8084	4535	·1	824·3427	2·916 1078
·2	799·5527	8471	·7	812·0870	6026	·2	824·6213	2546
·3	799·8312	9983	·8	812·3655	7515	·3	824·8998	4012
·4	800·1098	2·903 1496	·9	812·6441	9004	·4	825·1784	5478
14·5	800·3883	3008	19·0	812·9226	2·910 0492	23·5	825·4569	6944
·6	800·6668	4518	·1	813·2011	1980	·6	825·7354	8409
·7	800·9454	6029	·2	813·4797	3468	·7	826·0140	9874
·8	801·2239	7539	·3	813·7582	4953	·8	826·2925	2·917 1339
·9	801·5025	9049	·4	814·0368	6440	·9	826·5711	2802
15·0	801·7810	2·904 0557	19·5	814·3153	7927	24·0	826·8496	2·917 4265
·1	802·0595	2067	·6	814·5938	9411	·1	827·1281	5728
·2	802·3381	3574	·7	814·8724	2·911 0896	·2	827·4067	7191
·3	802·6166	5081	·8	815·1500	2380	·3	827·6852	8652
·4	802·8952	6589	·9	815·4295	3865	·4	827·9638	2·918 0114
15·5	803·1737	8095	20·0	815·7080	2·911 5347	24·5	828·2423	1574
·6	803·4522	9601	·1	815·9865	6830	·6	828·5208	3034
·7	803·7308	2·905 1106	·2	816·2651	8313	·7	828·7994	4495
·8	804·0093	2612	·3	816·5436	9794	·8	829·0779	5953
·9	804·2879	4116	·4	816·8222	2·912 1276	24·9	829·3565	7413
16·0	804·5664	2·905 5618	20·5	817·1007	2756	25·0	829·6350	2·918 8871
·1	804·8449	7122	·6	817·3792	4236	·1	829·9135	2·919 0329
·2	805·1235	8625	·7	817·6578	5716	·2	830·1921	1786
·3	805·4020	2·906 0127	·8	817·9363	7195	·3	830·4706	3242
·4	805·6806	1629	·9	818·2149	8674	·4	830·7492	4699

TABLE 11 (*continued*).

TABLE for Correction of Volumes of Gases—*continued.*

t	$760 \times (1 + \delta t)$.	Log. $[760 \times (1 + \delta t)]$.	t	$760 \times (1 + \delta t)$	Log. $[760 \times (1 + \delta t]$.	t	$760 \times (1 + \delta t)$.	Log. $[760 \times (1 + \delta t)]$.
25·5	831·0277	2·919 6155	27·0	835·2058	2·921 7935	28·5	839·3839	2·923 9607
·6	831·3062	7610	·1	835·4843	9384	·6	839·6624	2·924 1047
·7	831·5848	9065	·2	835·7629	2·922 0831	·7	839·9410	2488
·8	831·8633	2·920 0520	·3	836·0414	2279	·8	840·2195	3928
25·9	832·1419	1974	·4	836·3200	3725	28·9	840·4981	5368
26·0	832·4204	2·920 3427	27·5	836·5985	5172	29·0	840·7766	2·924 6806
·1	832·6989	4880	·6	836·8770	6616	·1	841·0551	8245
·2	832·9775	6333	·7	837·1556	8062	·2	841·3337	9683
·3	833·2560	7784	·8	837·4341	9507	·3	841·6122	2·925 1120
·4	833·5346	9236	27·9	837·7127	2·923 0951	·4	841·8908	2558
26·5	833·8131	2·921 0688	28·0	837·9912	2·923 2394	29·5	842·1693	3995
·6	834·0916	2137	·1	838·2697	3838	·6	842·4478	5431
·7	834·3702	3588	·2	838·5483	5281	·7	842·7264	6866
·8	834·6487	5038	·3	838·8268	6723	·8	843·0049	8301
26·9	834·9273	6487	·4	839·1054	8165	29·9	843·2835	9737
						30·0	843·5620	2·926 1170

TABLE 12.

Pressure of Aqueous Vapour in Millimetres of Mercury, from – 9·9° to + 35° C.

°	mm.	°	mm.	°	mm.	°	mm.	°	mm.	°	mm.
– 9·9	2·096	– 5·4	3·034	– 0·9	4·299	3·5	5·889	8·0	8·017	12·5	10·804
·8	·114	·3	·058	·8	·331	·6	·930	·1	·072	·6	·875
·7	·132	·2	·082	·7	·364	·7	·972	·2	·126	·7	·947
·6	·150	·1	·106	·6	·397	·8	6·014	·3	·181	·8	11·019
·5	·168	– 5·0	·131	·5	·430	3·9	·055	·4	·236	12·9	·090
– 9·4	·186	– 4·9	3·156	– 0·4	·463	4·0	6·097	8·5	·291	13·0	11·162
·3	·204	·8	·181	·3	·497	·1	·140	·6	·347	·1	·235
·2	·223	·7	·206	·2	·531	·2	·183	·7	·404	·2	·309
·1	·242	·6	·231	·1	·565	·3	·226	·8	·461	·3	·383
– 9·0	·261	·5	·257	– 0·0	4·600	·4	·270	8·9	·517	·4	·456
– 8·9	2·280	– 4·4	·283	+ 0·0	4·600	4.5	·313	9·0	8·574	13·5	·530
·8	·299	·3	·309	·1	·633	·6	·357	·1	·632	·6	·605
·7	·318	·2	·335	·2	·667	·7	·401	·2	·690	·7	·681
·6	·337	·1	·361	·3	·700	·8	·445	·3	·748	·8	·757
·5	·356	– 4·0	·387	·4	·733	4·9	·490	·4	·807	13·9	·832
– 8·4	·376	– 3·9	3·414	0·5	·767	5·0	6·534	9·5	·865	14·0	11·908
·3	·396	·8	·441	·6	·801	·1	·580	·6	·925	·1	·986
·2	·416	·7	·468	·7	·836	·2	·625	·7	·985	·2	12·064
·1	·436	·6	·495	·8	·871	·3	·671	·8	9·045	·3	·142
– 8·0	·456	·5	·522	0·9	·905	·4	·717	9·9	·105	·4	·220
– 7·9	2·477	– 3·4	·550	1·0	4·940	5·5	·763	10·0	9·165	14·5	·298
·8	·498	·3	·578	·1	·975	·6	·810	·1	·227	·6	·378
·7	·519	·2	·606	·2	5·011	·7	·857	·2	·288	·7	·458
·6	·540	·1	·634	·3	·047	·8	·904	·3	·350	·8	·538
·5	·561	– 3·0	·662	·4	·082	5·9	·951	·4	·412	14·9	·619
– 7·4	·582	– 2·9	3·691	1·5	·118	6·0	6·998	10·5	·474	15·0	12·699
·3	·603	·8	·720	·6	·155	·1	7·047	·6	·537	·1	·781
·2	·624	·7	·749	·7	·191	·2	·095	·7	·601	·2	·864
·1	·645	·6	·778	·8	·228	·3	·144	·8	·665	·3	·947
– 7·0	·666	·5	·807	1·9	·265	·4	·193	10·9	·728	·4	13·029
– 6·9	2·688	– 2·4	·836	2·0	5·302	6·5	·242	11·0	9·792	15·5	·112
·8	·710	·3	·865	·1	·340	·6	·292	·1	·857	·6	·197
·7	·732	·2	·895	·2	·378	·7	·342	·2	·923	·7	·281
·6	·754	·1	·925	·3	·416	·8	·392	·3	·989	·8	·366
·5	·776	– 2·0	·955	·4	·454	6·9	·442	·4	10·054	15·9	·451
– 6·4	·798	– 1·9	3·985	2·5	·491	7·0	7·492	11·5	·120	16·0	13·536
·3	·821	·8	4·016	·6	·530	·1	·544	·6	·187	·1	·623
·2	·844	·7	·047	·7	·569	·2	·595	·7	·255	·2	·710
·1	·867	·6	·078	·8	·608	·3	·647	·8	·322	·3	·797
– 6·0	·890	·5	·109	2.9	·647	·4	·699	11·9	·389	·4	·885
– 5·9	2·914	– 1·4	·140	3·0	5·687	7·5	·751	12·0	10·457	16·5	·972
·8	·938	·3	·171	·1	·727	·6	·804	·1	·526	·6	14·062
·7	·962	·2	·203	·2	·767	·7	·857	·2	·596	·7	·151
·6	·986	·1	·235	·3	·807	·8	·910	·3	·665	·8	·241
·5	3·010	1·0	·267	·4	·848	7·9	·964	·4	·734	16·9	·331

TABLE 12 (*continued*).

Pressure of Aqueous Vapour—*continued.*

°	mm.	°	mm.	°	mm.	°	mm.	°	mm.	°	mm
17·0	14·421	20·0	17·391	23·0	20·888	26·0	24·988	29·0	29·782	32·0	35·359
·1	·513	·1	·500	·1	21·016	·1	25·138	·1	·956	·1	·559
·2	·605	·2	·608	·2	·144	·2	·288	·2	30·131	·2	·760
·3	·697	·3	·717	·3	·272	·3	·438	·3	·305	·3	·962
·4	·790	·4	·826	·4	·400	·4	·588	·4	·479	·4	36·165
17·5	·882	20·5	·935	23·5	·528	26·5	·738	29·5	·654	32·5	·370
·6	·977	·6	18·047	·6	·659	·6	·891	·6	·833	·6	·576
·7	15·072	·7	·159	·7	·790	·7	26·045	·7	31·011	·7	·783
·8	·167	·8	·271	·8	·921	·8	·198	·8	·190	·8	·991
17·9	·262	20·9	·383	23·9	22·053	26·9	·351	29·9	·369	32·9	37·200
18·0	15·357	21·0	18·495	24·0	22·184	27·0	26·505	30·0	31·548	33·0	37·410
·1	·454	·1	·610	·1	·319	·1	·663	·1	·729	·1	·621
·2	·552	·2	·724	·2	·453	·2	·820	·2	·911	·2	·832
·3	·650	·3	·839	·3	·588	·3	·978	·3	32·094	·3	38·045
·4	·747	·4	·954	·4	·723	·4	27·136	·4	·278	·4	·258
18·5	·845	21·5	19·069	24·5	·858	27·5	·294	30·5	·463	33·5	·473
·6	·945	·6	·187	·6	·996	·6	·455	·6	·650	·6	·689
·7	16·045	·7	·305	·7	23·135	·7	·617	·7	·837	·7	·906
·8	·145	·8	·423	·8	·273	·8	·778	·8	33·026	·8	39·124
18·9	·246	21·9	·541	24·9	·411	27·9	·939	30·9	·215	33·9	·344
19·0	16·346	22·0	19·659	25·0	23·550	28·0	28·101	31·0	33·405	34·0	39·565
·1	·449	·1	·780	·1	·692	·1	·267	·1	·596	·1	·786
·2	·552	·2	·901	·2	·834	·2	·433	·2	·787	·2	40·007
·3	·655	·3	20·022	·3	·976	·3	·599	·3	·980	·3	·230
·4	·758	·4	·143	·4	24·119	·4	·765	·4	34·174	·4	·455
19·5	·861	22·5	·265	25·5	·261	28·5	·931	31·5	·368	34·5	·680
·6	·967	·6	·389	·6	·406	·6	29·101	·6	·564	·6	·907
·7	17·073	·7	·514	·7	·552	·7	·271	·7	·761	·7	41·135
·8	·179	·8	·639	·8	·697	·8	·441	·8	·959	·8	·364
19·9	·285	22·9	·763	25·9	·842	28·9	·612	31·9	35·159	34·9	·595
										35·0	827

Coefficients and Logarithms for Volumetric Analysis.

	Coefficients.		Logarithms.
Normal H_2SO_4	1 c.c. = 0·04904 gm.	H_2SO_4	$\bar{2}\cdot69055$
	,, = 0·04804 ,,	SO_4	$\bar{2}\cdot68160$
	,, = 0·04004 ,,	SO_3	$\bar{2}\cdot60249$
Normal HCl	1 c.c. = 0·03647 ,,	HCl	$\bar{2}\cdot56194$
	,, = 0·03546 ,,	Cl	$\bar{2}\cdot54974$
Normal HNO_3	1 c.c. = 0·06302 ,,	HNO_3	$\bar{2}\cdot79948$
	,, = 0·06201 ,,	NO_3	$\bar{2}\cdot79246$
	,, = 0·054 ,,	N_2O_5	$\bar{2}\cdot73239$
Normal $H_2C_2O_4$	1 c.c. = 0·06302 ,,	$H_2C_2O_4, 2OH_2$	$\bar{2}\cdot79948$
	,, = 0·045 ,,	$H_2C_2O_4$	$\bar{2}\cdot65321$
Normal Acid	1 c.c. = 0·01703 ,,	NH_3	$\bar{2}\cdot23121$
	,, = 0·03505 ,,	NH_4HO	$\bar{2}\cdot54469$
	,, = 0·191 ,,	$Na_2B_4O_710H_2O$	$\bar{1}\cdot28103$
	,, = 0·03705 ,,	Ca2HO	$\bar{2}\cdot56879$
	,, = 0·02805 ,,	CaO	$\bar{2}\cdot44793$
	,, = 0·05005 ,,	$CaCO_3$	$\bar{2}\cdot69940$
	,, = 0·08569 ,,	BaH_2O_2	$\bar{2}\cdot93293$
	,, = 0·15776 ,,	$BaH_2O_28H_2O$	$\bar{1}\cdot19800$
	,, = 0·09869 ,,	$BaCO_3$	$\bar{2}\cdot99427$
	,, = 0·02016 ,,	MgO	$\bar{2}\cdot30449$
	,, = 0·04215 ,,	$MgCO_3$	$\bar{2}\cdot62490$
	,, = 0·05611 ,,	KHO	$\bar{2}\cdot74904$
	,, = 0·0691 ,,	K_2CO_3	$\bar{2}\cdot83948$
	,, = 0·1881 ,,	$KHC_4H_4O_6$	$\bar{1}\cdot27448$
	,, = 0·1081 ,,	$K_3C_6H_5O_7,H_2O$	$\bar{1}\cdot03391$
	,, = 0·0981 ,,	$KC_2H_3O_2$	$\bar{2}\cdot99176$
	,, = 0·1411 ,,	$KNaC_4H_4O_6,4H_2O$	$\bar{1}\cdot14953$
Normal Acid	1 c.c. = 0·04 ,,	NaHO	$\bar{2}\cdot60206$
	,, = 0·053 ,,	Na_2CO_3	$\bar{2}\cdot72427$
	,, = 0·14308 ,,	$Na_2CO_310H_2O$	$\bar{1}\cdot15558$
	,, = 0·084 ,,	$NaHCO_3$	$\bar{2}\cdot92427$
Normal NaHO	1 c.c. = 0·040 ,,	NaHO	$\bar{2}\cdot60206$
	,, = 0·031 ,,	Na_2O	$\bar{2}\cdot49136$
Normal KHO	1 c.c. = 0·05611 ,,	KHO	$\bar{2}\cdot74904$
	,, = 0·0471 ,,	K_2O	$\bar{2}\cdot67302$
Normal Na_2CO_3	1 c.c. = 0·053 ,,	Na_2CO_3	$\bar{2}\cdot72427$
	,, = 0·030 ,,	CO_3	$\bar{2}\cdot47712$
	,, = 0·022 ,,	CO_2	$\bar{2}\cdot34242$
Normal Alkali	1 c.c. = 0·06 ,,	$HC_2H_3O_2$	$\bar{2}\cdot77815$
	,, = 0·07 ,,	$H_3C_6H_5O_7H_2O$	$\bar{2}\cdot84510$
	,, = 0·03647 ,,	HCl	$\bar{2}\cdot56194$
	,, = 0·0809 ,,	HBr	$\bar{2}\cdot90810$
	,, = 0·012793 ,,	HI	$\bar{1}\cdot10697$
	,, = 0·06302 ,,	HNO_3	$\bar{2}\cdot79948$
	,, = 0·04904 ,,	H_2SO_4	$\bar{2}\cdot69055$
	,, = 0·07503 ,,	$H_2C_4H_4O_6$	$\bar{2}\cdot87523$

	Coefficients.	Logarithms.
$^N/_{10}$ Silver Nitrate	1 c.c. = 0·010788 gm. Ag	$\bar{2}$·03294
	,, = 0·017 ,, $AgNO_3$	$\bar{2}$·23044
	,, = 0·003546 ,, Cl	$\bar{3}$·54974
	,, = 0·00535 ,, NH_4Cl	$\bar{3}$·72835
	,, = 0·007456 ,, KCl	$\bar{3}$·87251
	,, = 0·0119 ,, KBr	$\bar{2}$·07555
	,, = 0·01029 ,, NaBr	$\bar{2}$·01242
	,, = 0·0062 ,, Na_2HAsO_4	$\bar{3}$·79239
$^N/_{10}$ Iodine	1 c.c. = 0·003203 ,, SO_2	$\bar{3}$·50555
	,, = 0·004104 ,, H_2SO_3	$\bar{3}$·61321
	,, = 0·004948 ,, As_2O_3	$\bar{3}$·69443
	,, = 0·024822 ,, $Na_2S_2O_35H_2O$	$\bar{2}$·39484
	,, = 0·012609 ,, $Na_2SO_37H_2O$	$\bar{2}$·10068
	,, = 0·009714 ,, $K_2SO_32H_2O$	$\bar{3}$·98740
$^N/_{10}$ Dichromate	1 c.c. = 0·01519 ,, $FeSO_4$	$\bar{2}$·18156
	,, = 0·01699 ,, $FeSO_4H_2O$	$\bar{2}$·23019
	,, = 0·0278 ,, $FeSO_47H_2O$	$\bar{2}$·44404
	,, = 0·01158 ,, $FeCO_3$	$\bar{2}$·06371
	,, = 0·02316 ,, Fe_3O_4	$\bar{2}$·36474
	,, = 0·007185 ,, FeO	$\bar{3}$·85643
$^N/_{10}$ Thiosulphate	1 c.c. = 0·024822 ,, Sodium thiosulphate	$\bar{2}$·39484
	,, = 0·012692 ,, I	$\bar{2}$·10353
	,, = 0·003546 ,, Cl	$\bar{3}$·54974
	,, = 0·007992 ,, Br	$\bar{3}$·90266
CALCIUM (Ca = 40·09)		
1 c.c. $^N/_{10}$ permanganate	= 0·002805 gm. CaO	$\bar{3}$·44793
,, ,,	= 0·005005 gm. $CaCO_3$	$\bar{3}$·69940
,, ,,	= 0·00861 gm. $CaSO_4$, $2OH_2$	$\bar{3}$·93500
,, normal oxalic acid	= 0·0280 gm. CaO	$\bar{2}$·44715
Cryst. oxalic acid × 0·444	= CaO	$\bar{1}$·64738
Double iron salt × 0·07143	= CaO	$\bar{2}$·85388
CHLORINE (Cl = 35·46)		
1 c.c. $^N/_{10}$ silver solution	= 0·003546 gm. Cl.	$\bar{3}$·54974
,, ,,	= 0·005846 gm. NaCl	$\bar{3}$·76686
,, arsenious or thiosulphate solution	= 0·003546 gm. Cl	$\bar{3}$·54974
CHROMIUM (Cr = 52)		
Metallic iron × 0·3104	= Cr	$\bar{1}$·49186
,, × 0·5968	= CrO_3	$\bar{1}$·77586
,, × 0·878	= $K_2Cr_2O_7$	$\bar{1}$·94347
,, × 1·928	= $PbCrO_4$	0·28519
Double-iron-salt × 0·0443	= Cr	$\bar{2}$·64640
,, × 0·0853	= CrO_3	$\bar{2}$·93095
,, × 0·1253	= $K_2Cr_2O_7$	$\bar{1}$·09795
,, × 0·2754	= $PbCrO_4$	$\bar{1}$·43996
1 c.c. $^N/_{10}$ solution	= 0·003333 gm. CrO_3	$\bar{3}$·52284
,, ,,	= 0·0049 gm. $K_2Cr_2O_7$	$\bar{3}$·69020
COPPER (Cu = 63·57)		
1 c.c. $^N/_{10}$ solution	= 0·006357 gm. Cu	$\bar{3}$·80325
Iron × 1·138	= copper	0·05614
Double iron salt × 0·1622	= copper	$\bar{1}$·21005
CYANOGEN (CN = 26·01)		
1 c.c. $^N/_{10}$ silver solution	= 0·005202 gm. CN	$\bar{3}$·71617
,, ,,	= 0·005404 gm. HCN	$\bar{3}$·73272
,, ,,	= 0·013022 gm. KCN	$\bar{2}$·11468
,, $^N/_{10}$ iodine	= 0·003255 gm. KCN	$\bar{3}$·51255

Coefficients.	Logarithms.
POTASSIUM FERROCYANIDE (K_4FeCy_6, $3OH_2$ = 422·36)	
Metallic iron × 7·563 = cryst. potassium ferrocyanide	0·87869
Double iron salt × 1·080 = ,, ,, ,, ...	0·03342
POTASSIUM FERRICYANIDE ($K_6Fe_2Cy_{12}$ = 658·42)	
Metallic iron × 5·895 = potassium ferricyanide	0·77048
Double iron salt × 1·684 = ,, ,, ...	0·22634
N/10 thiosulphate × 0·03292 = ,, ,, ...	$\bar{2}$·51746
GOLD (Au = 197·2)	
1 c.c. normal oxalic acid = 0·0657 gm. gold	$\bar{2}$·81757
IODINE (I = 126·92)	
1 c.c. N/10 thiosulphate = 0·012692 gm. iodine	$\bar{2}$·10353
IRON (Fe = 55·85)	
1 c.c. N/10 permanganate, dichromate, or thiosulphate = 0·005585 Fe	$\bar{3}$·74702
,, ,, ,, ,, ,, = 0·007185 FeO	$\bar{3}$·85643
,, ,, ,, ,, ,, = 0·007985 Fe_2O_3	$\bar{3}$·90227
LEAD (Pb = 207·1)	
1 c.c. N/10 permanganate = 0·010355 gm. lead	$\bar{2}$·01515
1 c.c. normal oxalic acid = 0·10355 gm. lead	$\bar{1}$·01515
Metallic iron × 1·854 = lead	0·26813
Double iron salt × 0·265 = lead	$\bar{1}$·42325
MANGANESE (Mn = 54·93)	
MnO = 70·93. MnO_2 = 86·93.	
Metallic iron × 0·4918 = Mn	$\bar{1}$·69179
,, × 0·6350 = MnO	$\bar{1}$·80277
,, × 0·7783 = MnO_2	$\bar{1}$·89115
Double iron salt × 0·0907 = MnO	$\bar{2}$·95761
,, × 0·1112 = MnO_2	$\bar{1}$·04610
Cryst. oxalic acid × 0·6896 = MnO_2	$\bar{1}$·83860
1 c.c. N/10 solution = 0·003547 gm. MnO	$\bar{3}$·54986
,, ,, = 0·004347 gm. MnO_2	$\bar{3}$·63819
MERCURY (Hg = 200)	
Double iron salt × 0·5104 = Hg	$\bar{1}$·70791
,, × 0·6914 = $HgCl_2$	$\bar{1}$·83972
1 c.c. N/10 solution = 0·0200 gm. Hg	$\bar{2}$·30103
,, ,, = 0·0208 gm. Hg_2O	$\bar{2}$·31806
,, ,, = 0·0271 gm. $HgCl_2$	$\bar{2}$·43296
NITROGEN AS NITRATES AND NITRITES (N_2O_5 = 108·02. N_2O_3 = 76·02)	
Normal acid × 0·0540 = N_2O_5	$\bar{2}$·73239
,, × 0·1011 = KNO_3	$\bar{1}$·00475
Metallic iron × 0·3761 = HNO_3	$\bar{1}$·57530
,, × 0·6035 = KNO_3	$\bar{1}$·78068
,, × 0·3224 = N_2O_5	$\bar{1}$·50840
SILVER (Ag = 107·88)	
1 c.c. N/10 NaCl = 0·010788 gm. Ag	$\bar{2}$·03294
,, ,, = 0·016989 gm. $AgNO_3$	$\bar{2}$·23017
SULPHURETTED HYDROGEN (H_2S = 34·086)	
1 c.c. N/10 arsenious solution = 0·00255 gm. H_2S	$\bar{3}$·40654
TIN (Sn = 119)	
Metallic iron × 1·0654 = tin	0·02749
Double iron salt × 0·1522 = tin	$\bar{1}$·18241
Factor for N/10 iodine or permanganate solution 0·00595	$\bar{3}$·77452
ZINC (Zn = 65·37)	
Metallic iron × 0·5852 = Zn	$\bar{1}$·76733
,, × 0·7285 = ZnO	$\bar{1}$·86241
Double iron salt × 0·0836 = Zn	$\bar{2}$·92221
,, × 0·1041 = ZnO	$\bar{1}$·01745
1 c.c. N/10 solution = 0·003268 gm. Zn	$\bar{3}$·51428

ADDENDA AND CORRIGENDA.

Page 41. **Methyl Red.**—The colour changes of Methyl Orange and Methyl Red and the value of the latter as an indicator have been recently discussed by H. T. Tizard.* The author gives a method for the preparation of methyl red which is said to give higher yields than that recommended by Rupp and Loose. The author concludes that methyl red is greatly superior to methyl orange as indicator. Not only is the end-point very much sharper, but the neutral point so found is very much nearer the theoretical point than with methyl orange.

Page 142. **Determination of Chlorine by Mohr's Method.**—In the presence of much organic matter, or of sulphuretted hydrogen, the solution may be prepared for titration as follows :—

200 c.c. are warmed to about 100° C. and neutral potassium permanganate solution added in slight excess. After boiling for about five minutes if the colour is destroyed a little more permanganate solution is added. The excess of permanganate is then removed by adding a few drops of alcohol to the hot liquid, which, after standing for 15 minutes, is filtered, and the filtrate when cooled diluted to the original volume. The solution, which must be neutral, is then divided into two equal portions and titrated.

Page 154. **Antimony. Györy's Method.**
J. B. Duncan† recommends the following procedure.

He standardizes the $^N/_{10}$ potassium bromate solution by dissolving 0·3 gm. of pure finely divided antimony in 20 c.c. HCl and a few drops of bromine in a covered 400 c.c. beaker, keeping the liquid warm and occasionally shaking till the metal is dissolved. Then boil off excess of bromine, cool a little, and add about 0·75 gm. of sodium sulphite. Boil the mixture down to about half its volume to drive off SO_2. (In the case of alloys this latter operation will also remove any arsenic present.) Rinse the cover and sides of the beaker with hot water, and add a little HCl. Then heat the liquid to boiling and run in the decinormal bromate from a burette until nearly all the antimony has been oxidized. Now add three drops of methyl orange and continue the addition of bromate until the colour of the methyl orange is destroyed. About 50 c.c. will be required, as 1 c.c. of $^N/_{10}$ bromate = about 0·006 gm. Sb. The exact value of 1 c.c. is thus obtained. The process is strongly recommended for the analysis of hard lead, alloys, ores of antimony, etc. 0·3 gm. is taken for the determination,

* *J. C. S.* 1910, **97**, 3477–3490. † *C. N.* 1907, **95**, 49.

and solution is brought about as described above. The author recommends a process of fusion for difficultly decomposable substances.

Page 256. **Manganese. Fischer's Modification of Volhard's Method.**—Cahen and Little's critical examination of this method has been referred to in the text. Whilst this book has been issuing from the press, however, their paper has been published in full.* The authors find that a definite end-point cannot be obtained if the titration be carried out at a boiling temperature. They, therefore, vary Fischer's procedure slightly in the following manner:—After the first titration with permanganate and before the addition of acetic acid the solution is cooled under the tap for a minute or two, and after the addition of acetic acid the liquid is shaken thoroughly. The hot, but not boiling, solution is then further titrated with permanganate, added a few drops at a time, with vigorous shaking for half a minute after each addition, until the supernatant liquid retains its pink colour after being well shaken several times. This is the end-point of the titration. The quantities given in the text apply to 500 c.c. of solution. They find that the method agrees very satisfactorily with the bismuthate, gravimetric, and Pattinson's methods.

Page 256. Line 19, for "absorbed" read "adsorbed."

Page 390. **Formaldehyde. Legler's Method.**—Herrmann† has shown that the inaccuracies in Legler's method of determining formaldehyde by conversion into hexamethylenetetramine, which are due to the slow action of ammonia solution and the instability of standard ammonia solutions, may be obviated by developing ammonia gas within the liquid itself from ammonium chloride by the addition of standard sodium hydroxide solution. The heat of the reaction causes the nascent ammonia to convert the formaldehyde instantaneously and completely into hexamethylenetetramine. A weighed quantity (between 4 and 4·5 gm.) of ordinary formalin solution is mixed in a stoppered bottle of 150 to 200 c.c. capacity, with 3 gm. of pure finely-powdered ammonium chloride and then with 25 c.c. of 2N—sodium hydroxide solution added from a burette as rapidly as possible, and the bottle is closed and allowed to stand. As soon as its contents have cooled to the ordinary temperature, 50 c.c. of water and 4 drops of a 1 per cent. solution of methyl orange are introduced, and the liquid titrated with $^{N}/_{1}$ sulphuric acid, to obtain the number of c.c. of $^{N}/_{1}$ alkali solution consumed in the formation of the hexamethylenetetramine. The result multiplied by 0·06 gives the quantity of formaldehyde in grams in the formalin solution. The results thus obtained are closely concordant, and are practically identical with those given when the liquid is allowed to stand for 24 hours before the titration.

* *Analyst*, 1911, **36**, 52. † *Chem. Zeit.* 1911, **35**, 25.

Page 403. The most recent* "Saponification Values" for the oils named below are as follows :—

Lard	195–203
Horse fat	195–199
Lard Oil	193–198
Niger Oil	186–192
Linseed	190–201
Cotton Seed	191–196
Whale	184–194
Seal	190–193
Rape	170–175
Cod Liver	179–189
Castor	175–183
Sperm	120–137
Shark Liver	157–164

CORRIGENDA.

Page 19, line 10 from bottom.—For "a kilogram weight" read "999·13 grams."

Page 20, lines 2 and 10.—For "half a minute" read "a minute."

Page 28, last line but one.—For "$^N/$" read "$^N/_{10}$."

Page 35, line 26.—Insert * after "follows."

Page 64, line 20.—For "titratiug" read "titrating."
For "phenophthalein" read "phenolphthalein."

Page 65, last line.—For "finely-divided" read "reduced."

Page 74, last line but one.—For "at" read "as."

Page 82, line 39.—For 1 c.c. $AgNO_3$ 00 = ·54 gram HCy.
read 1 c.c. $^N/_{10}$ $AgNO_3$ = ·0054 gram HCy.

Page 88, line 17.—For "analyzed" read "analysed."

Page 88, 3 lines from bottom.—For Ronch se read Ronchèse.

Page 136, line 11.—For "p. 8" read "p. 225."

Page 222, line 7.— For "Schroder" read "Schröder."

Page 250, last line
Page 259, lines 33 and 37 } For "Fresenius' and Wills'" read "Fresenius and Will's."

Page 323, lines 20 and 36
Page 324, line 15
Page 337, last line
Page 338, line 8 } For "hydrolyzed" read "hydrolysed."

Page 326, last line.—For "dialyzer" read "dialyser."

Page 422, line 5 from bottom.—For "10" read "100."

Page 428, line 8 from bottom.—For "Felhing" read "Fehling."

Page 430, note.—For "*Z. A. C.*" read "*Z. a. C.*"

Page 462, line 9.—For "analyzed" read "analysed."

Page 585, line 13.—For $_4$ read ,

*See Allen's *Comm. Org. Analysis* 1910, Vol. II., pp. 69–73.

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(For List of Tables see Table of Contents.)

D = Determination.

wt 13 cm filter paper = 0.8079 g

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